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INTRODUCTION TO QUALITATIVE CHEMICAL ANALYSIS

BY

TH. WILHELM FRESENIUS

SEVENTEENTH EDITION

OF THE ORIGINAL WORK BY C. REMIGIUS FRESENIUS

TRANSLATED BY

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EDITOR OF "THE ANALYST"

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TRANSLATOR'S PREFATORY NOTE

THE seventeenth German edition of the standard work of Fresenius, which was first planned so far back as 1840, has been completely remodelled to make it conform with the modern conceptions of Chemistry. A chapter dealing with reagents, which appeared in former editions, has been omitted as being no longer necessary, whilst the notes and additions to the systematic course have been transferred to a separate chapter. At the same time, the principles of the analytical systems used in the course are made clearer by the addition of tables and general surveys of each stage.

It should be noted that in the English translation degrees of temperature are on the centigrade scale as in the German, and that the abbreviations of the titles of the scientific journals mentioned in the footnotes are those used by the English Chemical Society.

Miss Elliott, M.B.E., has given me much help in the long work of translating and seeing the book through the press, and I wish to thank her for her assistance.

C. AINSWORTH MITCHELL.

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INTRODUCTION

CHEMISTRY is the science which embodies our knowledge of the substances which compose the objects occurring in nature, their composition and decomposition, and above all their behaviour towards each other. A special branch of the subject is termed *Analytical Chemistry*, owing to its having as its specific aim the decomposition (analysis) of compound substances, and the identification of their constituents. If this determination of the constituents is only concerned with their nature the analysis is *qualitative*, but if the quantity of the individual components is required it is *quantitative*. The former has therefore for its aim the preparation of the constituents of an unknown substance into forms or conditions *already known*, so that these new forms or conditions may furnish definite proof of the presence of the individual component substances. The value of these methods depends upon two conditions: they must be firstly absolutely reliable, and secondly must attain the end in view as rapidly as possible. On the other hand, the aim of quantitative analysis is to effect the complete separation of the substances detected by the qualitative examination in forms which allow them to be gravimetrically determined as accurately as possible, or to effect their estimation by some other method.

The methods by which these different ends are attained are, as might be expected, very different. The study of qualitative and quantitative analysis must therefore be kept distinct, and the nature of the subject requires us to begin with the former.

To carry out qualitative investigations the primary essentials are a knowledge of the chemical elements and their most important compounds, and also of the fundamental laws of chemistry, whilst practice in the visualisation of chemical processes is necessary. Attention to detail, scrupulous cleanliness, and some skill in manipulation are also required, together with a corresponding training of the faculty of observation, so that no phenomenon which occurs may pass unnoticed. If to these requirements is also added the habitual practice, when results contrary to experience are obtained, of looking for an error in the experiment itself, or rather in the absence of a condition necessary for the production of the phenomenon, since this habit must be based on a firm belief in the immutability of the laws of nature, then all the conditions necessary for a fruitful study of analytical chemistry are present.

Now, although on the one hand chemical analysis is based on chemistry in general, and cannot be carried out without a knowledge thereof, yet, on the other hand, it must be regarded as a main support upon which the whole structure of the science rests; for it is of almost equal importance in all branches of chemistry, theoretical as well as applied, and its use to the practical chemist, the mineralogist and metallurgist, the pharmacist, the medical man, the rational agriculturist and others needs no amplification. But the essential condition upon which its being of use depends is that the results of the analyses made shall be absolutely trustworthy. And since this can only be obtained by thorough knowledge and painstaking practice, the general truth that a thing half known is more dangerous than ignorance must be regarded as especially applicable here, and a warning must be given against a superficial dabbling in chemical analysis.

For the solution of analytical problems not only theory but also practical work is necessary, and hence a knowledge of analytical chemistry cannot be acquired either by a purely theoretical study of the subject or by carrying out the methods in an absolutely detached manner; on the contrary, theory and practice must supplement each other in chemical analysis.

A qualitative investigation may be made with a twofold end in view; *viz.* either to prove whether a particular substance is or is not present in a material, as, for example, copper in an ore; or for the detection of *all* the constituents of a chemical compound or a mixture. Every substance may thus be an object for chemical analysis.

All the elements (see p. 2) are not of equal importance for practical chemistry. Only a number of them occurs widely distributed and in notable quantity in nature, and is of considerable technical importance. These are dealt with at length in this work.

The remainder are, in the main, only constituents of rare minerals, and only some of these are to a certain extent of technical importance, but may nevertheless be identified by the ordinary methods of qualitative analysis. These are discussed more briefly and in such a way that the study of their properties and their detection may be kept distinct from that of the more important elements. Other elements (such as the inert gases) are, it is true, widely distributed, but only in small quantities, whilst others (such as certain radioactive elements) have only a limited period of existence; and others again are almost identical with certain elements of common occurrence, and can only be distinguished from them by slight differences of atomic weight (see p. 2), as, for example, the different kinds of lead.

The three last classes of elements cannot be detected by the ordinary methods of qualitative analysis (with the limited exception of spectrum analysis). Hence they do not come within the scope of this book.

Chemical analysis demands, then, a knowledge of the *fundamental laws of general chemistry*, of *analytical operations*, and of the *behaviour of individual substances towards reagents*. Given these essentials, it is possible, with the aid of a *systematic procedure*, to undertake the investigation of unknown substances.

We deal, therefore, in the first part of this book with the above-mentioned preliminary essentials for a real qualitative analysis, and in the second part describe the systematic processes.

ERRATA

p. 9, line 6, read "are termed sulpho salts."

The headings to the undermentioned sections should read as follows:—

p. 587. Substances insoluble or dissolving with difficulty in water, but soluble in hydrochloric or nitric acids or *aqua regia.*

p. 599. Substances soluble in water, and substances insoluble in water but soluble in hydrochloric and nitric acids or *aqua regia.*

p. 670. II. In the presence of organic anions.

QUALITATIVE ANALYSIS

PART I.

CHAPTER I.

GENERAL CHEMICAL PRINCIPLES AND METHODS OF ANALYTICAL CHEMISTRY.

SEC. 1.

I. GENERAL FUNDAMENTAL CONCEPTIONS OF CHEMISTRY AND THEIR MODE OF PRESENTATION.

THE fruitful study and eventual self-reliant application of the methods of analytical chemistry demand a thorough knowledge of the fundamental chemical and physico-chemical laws of our science, which can be obtained from the numerous excellent text-books available. The primary aim of this short outline of the fundamental conceptions of chemistry and of the usual method of presenting them, which is given in the following paragraphs, is that the student, at every stage of his practical work in the laboratory, may have ready to his hand an explanation of the conceptions upon which he must base all his future work. We have deliberately refrained from assuming the student to have any prior knowledge, in order that this introduction may contain all that is necessary for understanding the following sections.

Some of the theoretical points can be more appropriately considered when describing special processes, and will, therefore, be dealt with in those places in following sections of this part.

Chemistry is the science of matter. *Chemical processes* are such as change not only individual properties (such as the rate of motion, temperature, etc.), but also *whole groups of properties*, and in such a way that there is not merely one individual substance present at the beginning and end, as is the case in the melting of ice, but so that in place of one or several individuals several new individual substances are produced, or *one* new individual substance from *several* substances.[1] For instance, in the calcining of limestone (calcium carbonate) carbonic acid (carbon dioxide) and lime (calcium oxide) are formed; the solution of zinc in sulphuric acid produces hydrogen gas and white vitriol (sulphate of zinc); in the roasting of hæmatite (iron oxide) with carbon metallic iron and carbonic acid (carbon dioxide) are produced; in the combustion of hydrogen with the oxygen of the air water is produced. By *individual* then in the *chemical sense* is to be understood not merely an external homogeneity, as, for example, the solution of sugar in water or the mixture of alcohol and water in which the quantities of the component constituents may vary within wide limits and their relative proportions may be varied at will within those limits—the definite properties of mixtures can also be changed by the proportion of the component parts of such mixtures *individual substances* in the *chemical sense* are rather those, which either cannot be decomposed into different substances, or those of which the component parts show *definite reciprocal quantitative relationship*. For instance, the relative weight of the above-mentioned substances, calcium oxide and carbon dioxide to calcium carbonate from which they arise, is 56·07 : 44 : 100·07. Substances which cannot be decomposed into other substances at will are called *fundamental substances* or *elements*.[2] Chemically individual substances consisting of several elements are called *chemical compounds*.

Individual chemical substances are composed of the smallest particles, incapable of further mechanical subdivision, which are all equal in a chemically individual substance, and that is to say are all of the same size; these are called *molecules*. As, however, the molecules of a definite kind of substance are all equal, whilst a compound can be decomposed into various elements, the compounds of molecules must consist of still smaller particles of the elements; these minute parts of elements are called *atoms*.

The atoms of each individual element are of absolutely similar nature, and therefore are all of the same size. *The weight of an atom is, therefore, of a constant magnitude*, characteristic of the element in question. An exact determination of the absolute weight of a single atom being impossible, only an approximate indirect estimation can be made. On the other hand, it is possible to determine accurately the reciprocal relationship of the weights of the atoms of the different elements.

---

[1] A chemical process can also exist when a new substance takes the place of an individual one, when it is not a question of alteration in the condition of aggregation (*e.g.* solid to liquid), but when the inner grouping and combination of the individual particles is different.

[2] For the sake of simplicity we adhere to this description, the unconditional validity of which cannot be maintained since the discovery of radio-active elements.

By fixing the weight of an atom of *one* element arbitrarily the reciprocal relationship of the masses of the atoms of different elements can be expressed in numbers (*atomic weights*) which are characteristic of each element. The atomic weight of oxygen$=16$ has been selected as the basis for the ordinary system.

The *molecules of elements* consist either of *one* or *more* atoms of the same kind;[1] thus metals, as a rule, contain one atom in the molecule, hydrogen two, etc. The *molecule of a chemical compound* is formed by the combination of *several atoms of different elements*. Each individual compound, however, contains a *definite* number characteristic of itself of the different atoms in the molecule; for instance, hydrogen chloride contains one atom of hydrogen and one of chlorine; water two atoms of hydrogen and one atom of oxygen; calcium carbonate one atom of calcium, one atom of carbon and three atoms of oxygen. This explains the fact that the quantity of the individual elements in individual compounds is in constant relationship, and that the reciprocal action of different compounds always occurs in *definite* quantitative proportions.

In combining with one another, atoms of individual elements show a *different degree* of combining power (*atomicity* or *valency*). Some elements, such as hydrogen, fluorine, sodium, are *monovalent*; they can only enter into combination in one way, they can only combine with one atom of another monovalent element: others, such as oxygen, sulphur, calcium, etc., are *divalent*; they can combine with *two* atoms of a *monovalent* element, or with *one* atom of another *divalent* element. This is called the equivalence of valencies. Other elements, such as aluminium, bismuth, etc., are *trivalent*; carbon, silica, etc., are *tetravalent*. A number of elements are of variable valency; for example, iron can be divalent or trivalent, copper monovalent or divalent.

Chemical formulæ are employed to represent the above-mentioned empirical facts, and the theory they are based upon, in a short and concise manner.

---

[1] The number of atoms in the molecule is a constant one for each individual element (according to its condition at the time). Thus ordinary oxygen contains two atoms in its molecule, ozone three, whilst the molecule of iodine vapour contains two atoms at temperatures below 600°, and only one atom above 600°.

The various elements are represented by distinctive capital letters, if necessary, with the addition of a small letter. (The first letters of the Latin names are used as symbols.) O=Oxygen (Oxygenum), H=Hydrogen (Hydrogenum), C=Carbon (Carbo), Cu=Copper (Cuprum), Cl=Chlorine, etc.

These letters represent not only the nature of an element, but also the size of one atom of the element. By combining the symbols of all elements present in a compound the formulæ of chemical compounds are obtained, *e.g.* HCl= Hydrochloric acid (spirits of salt), NaCl=Sodium chloride (common salt). The formula also expresses a quantity, namely, a molecule. If a molecule contains more than one atom of each element, the number of atoms is added to the symbols by means of small figures placed on a slightly lower level, for instance, H_2O=Water, Na_2O=Sodium oxide, H_2SO_4=Sulphuric acid. If the molecule of an element consists of several atoms it is represented accordingly, *e.g.* H_2=one molecule of hydrogen.

Chemical formulæ are also suitable for the graphic representation of the course of chemical processes. If several molecules of a substance take part in a reaction, their quantity is represented by a figure placed before the formulæ of the molecules.

The above-mentioned decompositions (see p. 2) are represented in formulæ as follows :-

Calcium carbonate is decomposed on ignition into calcium oxide and carbon dioxide :

$$CaCO_3=CaO+CO_2$$

Hydrogen burns with oxygen to form water :

$$2H_2+O_2=2H_2O$$

Zinc dissolves in sulphuric acid with the formation of zinc sulphate and the liberation of hydrogen :

$$Zn+H_2SO_4=ZnSO_4+H_2$$

Iron oxide and carbon yield metallic iron and carbon dioxide :

$$2Fe_2O_3+3C=4Fe+3CO_2$$

All these formulæ have *this* in common, that those on the left of the " equals " sign represent the substances present at the beginning of, and those on the right the substances that are the result of, the process. Hence it follows that all the atoms of each element that are on the left appear again on the right, but *neither more nor less.* Whilst the first of the above-mentioned formulæ shows only the decomposition of a molecule into two others, and the second shows the association of two elements to form a compound (*i.e.* by combination into a molecule), one can see from the third and fourth that the action of an element upon the molecule of a compound may cause the element to replace another element in the molecule, and consequently this second element to appear in the free condition.

In Formula 3 the divalent atom of zinc takes the place of the two monovalent atoms of hydrogen in the molecule of sulphuric acid, and so forms zinc sulphate.

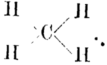
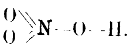
The fourth formula has been chosen purposely as being somewhat more complicated. In this case the tetravalent carbon acts on the oxide of the trivalent iron and replaces it in combination with oxygen. In order to represent this process it is necessary for three atoms of carbon (combining with six atoms of oxygen) to act on two molecules of iron oxide (combining with six atoms of oxygen).

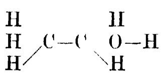
Another example is the process which consists of the fusion of heavy spar (barium sulphate) with soda (sodium carbonate), whereby barium carbonate and sodium sulphate are obtained:

$$BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$$

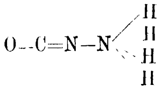
In this instance the metals barium and sodium, in other words the groups SO_4 and CO_3, exchange places in the molecules.

The individual atoms combine with each other within the molecule in a *definite* manner, corresponding to their valencies. The form of this combination may vary with the conditions.

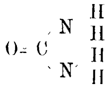
This construction of the molecules can also be expressed in a formula. The so-called structural formulæ are thus obtained. For instance, one atom of oxygen combines with two atoms of hydrogen $H-O-H$, one atom of carbon binds four atoms of hydrogen . One atom each of sodium, oxygen, and hydrogen is required to form sodium hydroxide, $Na-O-H$. One atom of nitrogen, three atoms of oxygen, and one atom of hydrogen form nitric acid . Two atoms of carbon, six atoms of hydrogen, and one atom of oxygen form alcohol C_2H_6O, or as a formula—



Substances which contain the same elements in equal proportions but in a different grouping are termed *isomeric*. Their differences can only be represented graphically by structural formulæ, *e.g.* ammonium isocyanate and urea are composed of one atom of carbon, one atom of oxygen, two atoms of nitrogen, and four atoms of hydrogen. They both have the same simple formula, CON_2H_4, but the difference can be expressed by the structural formulæ—



(or somewhat more simply $OCN—NH_4$), for ammonium isocyanate, and –



(or more simply $OC(NH_2)_2$) for urea. Ammonium isocyanate is transformed into urea when its aqueous solution is evaporated. From this example it can be seen that a *chemical* process may be involved in the transformation of *one* individual substance into *one* other individual substance when it is associated with a new grouping of the atoms of the molecule.

We can, therefore, replace the definition of chemical processes given on p. 1 by the following: Chemical processes are characterised by the fact that one or more individual substances replace one or more individual substances with molecules of different construction.

The structural formulæ, the use of which is of great importance in representing the inner construction of the molecules, and especially indispensable in organic chemistry, need not always be carried out to show all the separate details, but can often be used in a somewhat abbreviated form, as is the case in the example given of ammonium isocyanate and urea.

For the purpose of analytical chemistry it is mainly necessary to represent the reciprocal action of different molecules upon one another; as a rule it is not necessary to show the inner construction of the molecule in detail. We shall, therefore, only use structural formulæ when unavoidable, and as a rule in their abridged form.

Because in chemical processes different substances act upon one another in different ways, these reciprocal actions are termed *reactions*. In so far as a reaction is characteristic of a definite substance it can be employed for the identification of such substance. A substance which is used with another to produce a reaction (of identification) is termed a *reagent*.

A series of chemical substances of different kinds was mentioned in the examples dealt with above, and these are divided into classes according to their properties. A large number of elements belong to the *metal* class; as opposed to them there are the *non-metals* (metalloids), such as hydrogen, oxygen, nitrogen, sulphur, chlorine, etc.

Metals can combine on the one hand directly with a number of non-metals (*halogens*), chlorine, bromine, iodine, fluorine, and on the other hand with groups formed from non-metals and oxygen (acid radicles) to form salts: common salt (sodium chloride) $NaCl$, saltpetre (potassium nitrate) KNO_3, calcined gypsum (calcium sulphate) $CaSO_4$ anhydrous sodium carbonate Na_2CO_3.

These acid radicles, like the elements, also possess a definite valency, which therefore determines with how many atoms of a monovalent, or with what corresponding quantity of a polyvalent metal they can combine. If, for example, two monovalent acid radicles enter into combination with a divalent metal the acid radicle is enclosed in a bracket, after which the figure 2 is placed just below the line, *e.g.* barium nitrate $Ba(NO_3)_2$.

If the *halogens*, that is to say the *acid radicles*, combine with *hydrogen* instead of a metal, *acids* are produced, *e.g.* hydrochloric acid HCl, sulphuric acid H_2SO_4, nitric acid HNO_3. If the halogens combine with the (monovalent) radicle of water, hydroxyl OH, *hydroxides*, also termed *bases*, are formed, *e.g.* KOH, $Ba(OH)_2$, etc. The compounds of the elements, especially those of metals, with oxygen are termed *oxides*. Salts in which only the metal is in combination with acid radicle are termed *neutral*, *e.g.* K_2SO_4;[1] salts in which in addition to the metal there is also hydrogen in combination with the acid radicle are termed *acid* salts, *e.g.* $KHSO_4$.[2] Salts in which oxygen or hydroxyl in addition to the acid radicle are combined with the metal are termed *basic*, *e.g.* $BiOCl$, basic bismuth chloride or bismuth oxychloride; $Fe(OH)(SO_4)$, basic ferric sulphate.[1]

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[1] Neutral salts contain the same number of valencies of metal and acid radicle in combination with each other.

[2] In naming particular acid salts it is customary to use terms such as potassium hydrogen sulphate for $KHSO_4$, or disodium hydrogen phosphate for Na_2HPO_4, in order also to give expression in the name to the fact that the hydrogen and the metal stand in the same relationship towards the acid radicle.

If metals combine to form compounds with different valencies, as *e.g.* iron, which forms both monovalent and divalent compounds such as an oxide, hydroxide, and salts, the compounds with the metal in the lower state of valency are distinguished by affixing the syllable "ous" to the root of the Latin name; whilst those compounds in which the metal is present in the higher state of valency are characterised by affixing the syllable "ic," as, for example, ferrous oxide FeO, ferrous hydroxide $Fe(OH)_2$, ferrous sulphate $FeSO_4$, ferric oxide Fe_2O_3, ferric chloride $FeCl_3$, ferric hydroxide $Fe(OH)_3$, manganous chloride $MnCl_2$, manganic oxide Mn_2O_3.

Salts consisting of a metal and non-metal are designated by adding the syllable "ide" to the Latin root of the non-metal, *e.g.* sodium chloride $NaCl$. Salts with an acid radicle containing oxygen are described by names which are formed by attaching the syllable "ate" to the root of the Latin name of the non-metal in the acid radicle, as, for example, "sulphate" for salts with the acid radicle SO_4, "nitrate" for salts with the acid radicle NO_3. If a non-metal forms acid radicles with *different* quantities of oxygen, those *richer* in oxygen are designated by adding the syllable "ate," and those *poorer in oxygen* by the addition of the syllable "ite," *e.g.* potassium nitrate KNO_3, potassium nitrite KNO_2. If compounds are also formed with acid radicles containing yet other proportions of oxygen, those most important and of most frequent occurrence are distinguished in the way described, whilst those containing a higher proportion of oxygen receive the prefix "super" or now almost invariably "per," and those with a smaller proportion of oxygen the prefix "hypo," *e.g.* potassium chlorate $KClO_3$, potassium chlorite $KClO_2$, potassium perchlorate $KClO_4$, potassium hypochlorite $KClO$.

In the case of the acids it is customary not to say hydrogen chlorate, etc., but "chlor" acid, and then to distinguish between them, *e.g.* chloric acid $HClO_3$, chlorous acid $HClO_2$, perchloric acid $HClO_4$, and hypochlorous acid $HClO$.

By the combination of non-metals with oxygen, compounds may be produced which correspond to acids, but which are distinguished from them by the fact that they contain the elements of one or more molecules of water less than the acids; they are, therefore, termed acid *anhydrides*, *e.g.* sulphuric anhydride SO_3, corresponding to sulphuric acid H_2SO_4.[1]

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[1] For further details regarding salts, acids, and bases, see Sec. 3, in particular, p 25 *et seq.*

Compounds of the elements with sulphur are termed sulphides. Analogous to the oxygenated acid radicles there are also sulpho acid radicles, in which sulphur takes the place of oxygen. Compounds of these sulpho acids with metals are termed sulpho acids, *e.g.* sodium sulpho-arsenate Na_3AsS_4. Compounds of metals with the monovalent hydrogen sulphide radicle, corresponding to the hydroxyl radicle, are termed hydrosulphides, as, for example, KSH.

As mentioned above, in the formation of salts or acids there is a combination either of certain non-metallic elements (which are, therefore, also termed halogens or "salt formers") or of acid radicles composed of groups of elements containing oxygen with metals or with hydrogen. Combinations of elements, as *e.g.* the group NO_3 (the nitrate radicle), here play the same part as elements, *e.g.* chlorine. Such a relationship may also occur in quite a different manner. Thus other elementary groups may combine with hydrogen and metals

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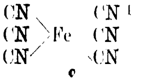
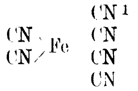
[1] Mention may here be made of the older conception and the method of expressing it, which at the present time is still frequently met with in everyday life.

The anhydrides of acids of to-day were formerly termed acids. Thus carbon dioxide (carbonic anhydride) CO_2 was called carbonic acid, silicic anhydride SiO_2, silicic acid, etc., and the formation of salts was regarded as being a combination of these acids (now termed anhydrides of acids) with the oxygenated compounds of metals. Copper sulphate, for example, was looked upon, not, as is now our practice, as being produced from copper and the sulphuric acid radicle $CuSO_4$, but from sulphuric "acid" and copper oxide; hence the formula was written CuO,SO_3, and the salt termed the sulphate of copper oxide. The description of the metallic oxide as base, *i.e.* basic substance of the salt, is also in accordance with this designation of the salt, with the name of the metallic oxide as the principal word, and that of the acid as the distinguishing epithet. With the change in our conceptions the use of the word "base" has also been dropped. At the present time only the *hydroxides* of metals (and of groups such as ammonium, which behave in an analogous manner) are still, strictly speaking, termed bases.

In this older mode of expression compounds in which the metals were present in different states of valency, *i.e.* in combination with different proportions of oxygen, chlorine, etc., were distinguished by prefixing the syllable "proto" to the name of the metalloid. Thus, as a rule, the compounds which we now designate ferrous, cuprous, etc., compounds were termed protoxide, protochloride, protosulphide, etc., and those which we now term ferric, cupric, mercuric, etc., compounds were known as oxides, chlorides, cyanides, etc. In the case of acids a distinction was drawn between those, the compounds of which to-day we designate by the termination "ite," and those to which we append the syllable "ate"; the former were known as phosphorous acid, sulphurous acid, etc., and the latter as sulphuric acid, phosphoric acid, etc. For example, ferrous sulphate $FeSO_4$, was termed the sulphate of protoxide of iron FeO,SO_3, calcium sulphite $CaSO_3$, sulphite of lime (or sulphite of calcium oxide) CaO,SO_2. For the compounds of a metal and a metalloid the names were formed by associating the names of the metal and non-metal, *e.g.* chloride of sodium NaCl, sulphide of lead PbS to form acids and salts, as *e.g.* cyanogen CN as the cyanide radicle, the trivalent group $Fe(CN)_6$ as the ferricyanide radicle



and the tetravelant group $Fe(CN)_6$ as the ferrocyanide radicle



The group NH_4, ammonium, plays the same part as a metal towards acid radicles, forming with them ammonium salts, which in all respects correspond to the salts of metals.

So long as such an elementary group takes part in reactions without undergoing decomposition it exhibits definite properties which are characteristic of it, and an element contained in it therefore shows other phenomena than when it is not combined in such a group. Thus, for example, the salts of chlorine (chlorides), when they come in contact with silver nitrate in solution, form silver chloride, which separates as a solid substance, whilst chlorine, when it is combined with three oxygen atoms to form the chlorate radicle does not cause such a separation, because silver chlorate is not insoluble.

An influence of this kind is seen to a still greater extent in the examples quoted above of ferri- and ferrocyanides, in which the *metal* iron combines with six cyanogen groups to form an acid radicle, which can thus also combine as a non-metal (like chlorine) with other metals to form salts (including iron present as a metal), *e g* potassium ferrocyanide $K_4Fe(CN)_6$ or ferric ferrocyanide $Fe_4[Fe(CN)_6]_3$

If elements (as in this case iron) or elementary groups (as in this case cyanogen), which can also by themselves form a constituent of a salt, unite to form a new group (which again can occur as the component of a salt), such compounds are termed *complexes*. Thus the ferro- or the ferricyanide radicles are complex groups, whilst the ferro- and ferricyanides are complex salts.

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[1] In the ferricyanide radicle trivalent iron is in combination with three cyanogen groups, and in the ferrocyanide radicle divalent iron is combined with two cyanogen groups, by means of the ordinary valencies. Moreover, in the first case there are three additional, and in the second case four additional combined cyanogen groups, which can only share one valency respectively, being attached (according to Werner's theory) by the so-called subsidiary valencies, indicated in the formulæ by dotted lines. (*Cf.* A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*, 3rd Ed. *Die Wissenschaft*, 8 Bd. Braunschweig, 1913.)

Further examples of such complex compounds are: ammonium phosphomolybdate $(NH_4)_3PO.12MoO_3$ (where there are twelve molecules of molybdic anhydride with one molecule of phosphate radicle united to form a complex acid radicle); potassium silicofluoride K_2SiF_6 (in which, as in the case of cyanogen, two metalloids are united to form an acid radicle); potassium cobaltinitrite $K_3Co(NO_2)_6$ (in which one atom of trivalent cobalt is united with six nitrite radicles to form a trivalent acid radicle); silver ammonium chloride $Ag(NH_3)_2Cl$ (in which case two ammonia molecules are united with one silver atom as a complex, which in this salt behaves like a metal).

In addition to these complex compounds, in which the complex appears as a simple metal or as an acid radicle in an inner form of combination, and in which we thus have only *one* molecule, though a complex one there are also compounds which frequently occur where the *molecules* are in an *inner form of combination*. To this class belong the *double salts*, *e g* potassium or ammonium sulphate combined with cupric, manganous, cobaltous, ferrous, etc., sulphates, typified by $(NH_4)_2SO_4,MnSO_4$, the alums, such as $K_2SO_4.Al_2(SO_4)_3$, and above all the compounds of salts (and other forms of combination) with water, the hydrates, such as $Cr(OH)_3 + 2H_2O$, in which two molecules of water are united with the chromic hydroxide in an inner form of combination. A particular class of these compounds with water includes those in which the water is present in the form of the so called water of crystallisation, *e g.* sodium carbonate in which ten molecules of water are in combination in the form of crystallised "soda." It was at one time frequently customary to represent these compounds containing water of crystallisation in such a way that one molecule of water of crystallisation was written as "aq" (from aqua), and a "plus" sign added, as, for example, $Na_2CO_3 + 10aq$.

The reactions between different substances may take place not only in one direction; for example, calcium carbonate may not only be decomposed into lime and carbon dioxide, but these two substances may also reunite. Such cases of *reversible reaction* may be expressed in a formula, as, for example, $CaCO_3 \rightleftarrows CaO + CO_2$.

As a matter of fact the decomposition by heat of calcium carbonate also takes place as an inner reaction, but only up to a certain limit, depending upon the temperature, for up to that point the proportions of carbon dioxide and calcium oxide present are such, that there is a simultaneous re-formation of as much calcium carbonate as is decomposed.

Both processes occur side by side, and it is only the difference between that which predominates and that which is less complete in its action which we observe as an alteration of the whole system. The ratio between the quantity of substance decomposed and the time in which this decomposition takes place is termed the *velocity of reaction*. When the velocity of reaction in both directions is of the same magnitude, so that there can be no predominance in either direction, the velocity of reaction of the whole system is *nil;* there is chemical equilibrium, and the reaction does not proceed further in either direction. The velocity with which a reaction follows *one* particular course depends upon various conditions, such as, for example, the temperature, the presence of other substances, and, above all, the relative quantities of the substances concerned in the reaction, *i.e.* on the concentration in the case of solutions and gases. Strictly speaking, *all* processes take place in both directions, but in many cases the velocity in one direction is almost infinitely small. Then the reaction takes place almost completely in the reverse direction. The practical result is that the latter alone is effective. This is notably the case when one of the products of the reaction is removed from the system, so that the amount of substances acting in the opposite direction is practically nil. When, therefore, in the above-mentioned example of the heating of calcium carbonate the gaseous carbon dioxide escapes into the air, the primary condition for a process in which the reaction expressed by the equation $CaCO_3 \rightleftarrows CaO + CO_2$ to proceed in the direction from right to left (viz. that both of the components to the right shall simultaneously be present) no longer exists (or not to any extent), so that the reaction practically proceeds entirely from left to right.

The equation $CaCO_3 = CaO + CO_2$ gives expression to this notion of a reaction proceeding in one direction only.

Another way in which a product of a reaction can be withdrawn from a decomposing system is by the *separation of an insoluble precipitate* from the solution containing the reacting substances. Solutions of silver nitrate and sodium chloride act upon one another as a reaction proceeding from both directions, with the formation of silver chloride and sodium nitrate: $AgNO_3 + NaCl \rightleftarrows AgCl + NaNO_3$. But since the silver chloride produced is very sparingly soluble, it separates almost completely, leaving only a practically negligible trace of silver in solution, so that an appreciable reaction in the direction of right to left cannot take place; the reaction thus proceeds practically throughout in the direction: $AgNO_3+NaCl = AgCl+NaNO_3$.[1]

Hence for the separation of the different substances which are present together, analytical chemistry employs processes in which one of the substances is separated in an insoluble or volatile form; in other words, processes which proceed practically only in one direction and to finality.

When this is not the case, but when both reactions can actually take place with appreciable speed, the conditions of equilibrium can be more readily followed, and in this respect it has been found that the laws of preponderance may be expressed in a simple mathematical form Thus the vapour of ammonium chloride on heating is decomposed into hydrogen chloride (hydrochloric acid) and ammonia. The reaction also takes place in the reverse direction, and is thus expressed by the formula $NH_4Cl \rightleftarrows NH_3+HCl$.

The process is completed up to a certain point as an inner reaction, which depends upon the temperature In this reaction the product of the substances formed by the decomposition stands in a certain definite relation to the quantity of the undecomposed ammonium chloride: $[NH_3][HCl]=K.[NH_4Cl]$ or also $\frac{[NH_3][HCl]}{[NH_4Cl]}=K$,[2] in which K is thus a constant (the equilibrium constant), depending upon the nature of the interacting substances and the temperature.

If a certain quantity of ammonia gas is already present where the above-mentioned process is taking place, it checks the decomposition of the ammonium chloride, because this ammonia as well as that formed by the decomposition of the ammonium chloride results in the product ammonia + hydrogen chloride.

This law of preponderance is termed the *law of mass action*, and can be expressed in a general formula in the following manner:—

The velocity of reaction, as Guldberg and Waage have found, is proportional to the masses entering into reaction, that is to say, in the cases of solutions and gases it is proportional to the concentration.

In the case of a reversible reaction in accordance with the simple scheme

$$A+B \rightleftarrows C$$

it follows that if the concentration of the substances A and B is designated as (A) and (B), *i.e.* the number of grammes of A and B in 1000 parts by volume, then the velocity v_1 for the course of the reaction from left to right is represented by

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[1] See Sec. 5.

[2] The use of square brackets denotes that it is not a molecule which is indicated by the formula, but the quantity of the compounds in question associated with the reaction.

$$v_1 = k_1[A].[B]$$

Correspondingly the velocity of reaction v_2 for the course of the reaction from right to left is expressed by

$$v_2 = k_2[C]$$

where $[C]$ represents the concentration in relation to the substance C, whilst k_1 and k_2 are constant proportional factors, the reaction velocity constants of both reactions.

When the velocity in one direction has become equal to that in the other direction equilibrium ensues, *i.e.* the reaction stops. This is the case when $k_1[A].[B] = k_2[C]$.

From this equation it follows that

$$\frac{[A].[B]}{[C]} = \frac{k_2}{k_1} = K$$

K is the quotient of the two constant velocities of reaction, that is to say, a constant itself, the so-called *equilibrium constant* of the reactions in question. It is dependent upon the nature of the substances, which either enter into reaction, or are formed during reaction, or upon the temperature, pressure, solvent, and other substances which may be present.

The law of mass action considered in relation to the reaction

$$n'A' + n''A'' + n'''A''' + \ldots = m'B' + m''B'' + m'''B''' + \ldots$$

may be expressed in a general form by the equation

$$\frac{[A']^{n'}.[A'']^{n''}.[A''']^{n'''} \ldots}{[B']^{m'}.[B'']^{m''}.[B''']^{m'''} \ldots} = K$$

where n and m represent how many molecules of the substances A and B enter into reaction or are produced by it.[1]

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[1] Further descriptions of a general chemical nature, and of their representation in formulæ, are given in the following sections on the analytical operations, especially in Sec. 3, because they can be more readily understood after the descriptions given there.

SEC. 2.

II. ANALYTICAL OPERATIONS.

General Outline.

THE identification of the substances to be investigated by analytical analysis may be effected either by direct observation of definite characteristic properties, when they can be immediately recognised in the substance under examination, or it requires, as mentioned above, that conditions shall be brought about under which such characteristic properties appear. The methods which are used for this purpose are termed analytical operations

These may be concerned either with the sharpening or differentiation of the sense perceptions, or with their amplification by the numerical determination of certain properties, as, for example, by the use of the microscope or spectroscope, or by the determination of the melting point, boiling point, specific gravity, etc. On the other hand, they may be concerned with the conversion of the substances under examination into characteristic forms or compounds, the properties of which, as, for example, the colour, crystalline form, etc., may be used for their identification.

If several substances are simultaneously present, the identification of one of them may often be interfered with by the presence of the others, because its specific properties cannot then be so clearly perceived; it is, therefore, one of the main tasks of analytical chemistry to separate several substances simultaneously present from one another so as to be able to identify them individually.

If a *heterogeneous* mixture of different dissimilar substances is present, as, for example, one of common salt and sand, or a liquid in which a solid body is distributed or has subsided, or a mixture of two fluids such as oil and water, the different substances which already are distinct from one another, *i.e.* the *phases*, can be directly separated from one another by mechanical means.[1] But if a chemical combination is present, or a "homogeneous" mixture (as, for example, a mixture of gases like air, a mixture of water and alcohol, a salt solution, or an alloy such as brass), it is necessary first to convert such a homogeneous substance into a heterogeneous mixture (into several phases) before it is possible to separate its individual constituents from one another by mechanical means. This conversion into a heterogeneous mixture is frequently accompanied by a simultaneous chemical decomposition, in which, for example, a constituent of a homogeneous substance is converted into another chemical compound, which is then separated in the form of a new phase. Thus silver can be separated from an aqueous solution of silver nitrate by converting it into insoluble silver chloride by, *e.g.* the addition of sodium chloride.

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[1] Phases are defined as forms of matter of the same kind, which are separated from each other by homogeneous surfaces. Thus a mixture of water and ether consists of two separate phases, as does also the mixture of metal powder and sand covered with water, whilst the mixture of these two solid substances with the air which is in between them represents a mixture of three phases. A solution of a solid substance or gas in a liquid forms one phase; if a portion of the solid substance separates from the solution (as on the cooling of the solution), or if some of the gas escapes (*e.g.* as in the opening of a soda-water bottle), then in addition to the liquid phase (the solution) a solid or gaseous phase is produced in the form of crystals or gas bubbles which separate.

Of the methods applicable to the separation, as thus defined, of different substances, those mainly used for analytical purposes, are the following: Solution, crystallisation, precipitation (with its subsequent subsidiary operations of filtration, decanting, and washing), dialysis, extraction by shaking, distillation, ignition, sublimation, melting, including disintegration by fusion, and explosive fusion.

In addition to these methods of separation, during which distinctive phenomena may appear, whereby the substances in question may at once be recognised, a series of identification tests is described, together with the apparatus and instruments for the purpose of making them, as also for the purpose of making separation tests. These include oxidation and reduction, determination of the reaction by means of indicators, gas production, burners and lamps, the blowpipe, application of bead tests, the spectroscope, and the microscope. No description is given here of quantitative physical methods, such as the determination of the density, the refractive indices, the solubility, or of such quantitative chemical estimations (as, for example, the iodine absorption of fats), the results of which can be used for the identification of substances, because a description of such methods comes under the heading of quantitative analysis, and they are not used in strictly qualitative analysis.

SEC. 3.

1. Solution.

One of the most important means of separating different substances from one another is solution, which can affect one substance but not another, or, on the other hand, may cause the separation of a substance previously in solution (together with others) in a solid or gaseous form.

But in addition to this, solution is important, because an intimate reciprocal contact is necessary to develop the action of different substances upon one another, and the mixing of two solutions is a particularly easy means of attaining this. By far the largest proportion of reactions takes place in solution (*corpora non agunt nisi fluida*). The solution of substances is therefore frequently a preliminary condition for the production of further reactions.

By solutions in the widest sense is understood all homogeneous mixtures of substances of a different kind. In the narrower sense, as primarily used here, solutions are understood to be fluid mixtures of this kind, and the process of solution of a gas in a liquid is termed *absorption*, that of a liquid in another liquid *mixture*, and only the solution of solid substances in a liquid is somewhat inaptly called *solution*. Two processes of solution may be distinguished. In the simplest case, *e.g.* in the solution of sodium chloride in water, the dissolved substance may be recovered unchanged by the evaporation of the solvent This kind of solution is frequently termed physical solution. But a chemical reaction may also take place between the dissolved substance and the solvent, so that on removing the latter a different substance is obtained from that which was originally dissolved. For instance, when chalk is dissolved in hydrochloric acid a liquid is obtained which, on evaporation, leaves calcium chloride. Such a process is frequently termed chemical solution.

In all solutions of solid substances, or of gases in liquids, and in many cases in the solution of liquids in liquids, only a certain quantity of the substance undergoing solution can be dissolved by a definite quantity of solvent. A solution in which this relationship is reached is termed *saturated*. Solutions in which a smaller quantity of the substance than this is dissolved are known as unsaturated or dilute.

The ratio of the quantity of dissolved substance to the volume of solution is termed its *concentration* (numerically expressed, the concentration indicates the number of grammes of dissolved substance in a litre of solution). Solutions of higher concentration are also inaptly called "concentrated," those of lower concentration "dilute." The quantity of substance dissolved at the saturation point depends upon the temperature; hence one can only say that a solution is saturated at a definite temperature. In the solution of solid substances the quantity which can be taken up by a definite amount of liquid as a rule increases with the rise in temperature, whilst in the solution of gases the reverse is the case. If a chemical reaction is involved in the solution, the maximum quantity of substance dissolved depends not only on the saturation point, but also on the amount of the reagent which effects the solution. Thus the quantity of zinc which can be dissolved by a definite amount of sulphuric acid depends on the one hand on how much zinc sulphate a saturated solution can contain, and on the other, upon the quantity and concentration of the sulphuric acid, because when all the sulphuric acid originally present has been used in the formation of zinc sulphate no more zinc can be dissolved, even when the solution is not yet saturated with zinc sulphate

The more finely divided is a substance the more rapidly it is dissolved in a liquid, because it then can offer a greater surface for the solvent to attack. Shaking or stirring promotes solution, because the concentrated solution which forms in the neighbourhood of the solid substance is diluted with fresh solvent Heating usually promotes the solution of solid substances by increasing the solvent action.

Solutions of solid substances (which here are the primary consideration) are usually obtained in chemical laboratories by digesting the substances with the liquid in beakers, boiling flasks, test-tubes, or dishes, *i e.* by bringing them into contact for some time at the ordinary temperature, or by heating them).[1] In the case of chemical solutions it is as a rule best to bring the substance to be dissolved into contact with water (or with what other indifferent liquid is used), and then gradually to add the chemically active substance. In this way a large excess of the latter is avoided, too violent action is prevented, and solution takes place readily and completely.

The principal solvents used in qualitative analysis are the following: Firstly, *water.* It is always used in the form of distilled water, whenever in this book water is mentioned without further qualification, distilled water is always meant.

Secondly, *acids*, which include (1) hydrochloric acid usually in dilute form of sp. gr. 1·12, sometimes as concentrated acid of sp. gr. 1·17, and less frequently of sp. gr. 1·19. (2) Nitric acid, dilute of sp. gr. 1·2, concentrated of sp. gr. 1·4, and fuming acid of sp. gr. 1·47—1·5. (Red fuming nitric acid contains nitrous acid.) (3) *Aqua regia*, a mixture of one part of dilute nitric acid and three to four parts of dilute hydrochloric acid. (4) Sulphuric acid, dilute of sp. gr. 1·11, and concentrated of sp. gr. of 1·842.

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[1] For further details, see the second part, *Systematic Course of Qualitative Analysis*, rubric number 31. The solution of solid substances in continuous extraction apparatus is of more importance for quantitative estimations. It is described in the introduction to quantitative analysis.

Finally, *organic solvents*, including (1) alcohol (86 per cent. by weight and absolute), and (2) *ether*.

The physical properties of solutions of different substances in the same solvent at equal concentration, *i.e.* when equal weights of the dissolved substance are present in equal quantities of liquid, differ from one another, but if solutions are compared which in the same solvents contain as many molecules of the dissolved substance in an equal volume, it will be found that they all have a number of properties in common.

Thus the freezing and boiling points[1] (*i.e.* the temperature at which the solvent is converted into solid form, or separates as vapour even within the liquid itself), and, speaking generally, the vapour pressure of the solvent is the same for all such liquids. This also applies to the *osmotic pressure* (*i.e.* the force with which a dissolved substance attracts further solvent to itself (*Cf.* pp. 13-15).

To this law, however, a whole series of apparent exceptions is to be found in the aqueous solutions of those substances, salts, acids, and bases (metallic hydroxides), with which analytical chemistry is especially concerned.[2] They show vapour pressures (and, therefore, boiling and freezing points) and osmotic pressures, which correspond to a greater number of dissolved molecules than are actually present.

Solutions in which this deviation from the general rule occurs conduct an electric current, the dissolved substance being thereby decomposed. This process of chemical decomposition under the influence of an electric current is termed *electrolysis*, and the substance thereby decomposed an *electrolyte*.

The explanation for the behaviour of these solutions is to be found in the fact that on the solution of electrolytes there results a decomposition (*dissociation*) of a more or less considerable part of the dissolving molecules into metal (or a group with a corresponding behaviour, *e.g.* ammonium) or hydrogen, on the one hand, and into an acid radicle, or hydroxyl (OH) on the other hand. These fractions of the molecules originally dissolved behave in solution like complete molecules. If the sum of the undecomposed molecules and fractions of molecules in the solution is taken into consideration, such a solution shows normal vapour pressure and osmotic pressure."

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[1] Provided that on heating or cooling the liquid these temperatures can be reached without previous separation of the dissolved substance.

Hence in cases where the dissolved substance has also an appreciable vapour pressure of its own, *e.g.* solutions of gases and liquids, this relationship is less simple.

[2] This deviation may also occur in other, but not in all solvents.

The ratio of the sum of the dissolved molecules and fractions of molecules to the volume of the solution is termed the *osmotic concentration*, and the above-mentioned law of proportion may therefore be expressed as follows: Solutions of equal osmotic concentration show the same vapour pressure and osmotic pressure (and therefore the same freezing and boiling points).

The decomposition of molecules into metal and acid radicle in the process of solution is associated with the fact that the positive and negative electric charges reciprocally balancing each other in the original molecule, occur as separate charges in the fractions of the molecule, and in such a manner that the metals or hydrogen show a positive, and the acid radicle or hydroxyl a negative charge.

When an electric current is conducted into a solution containing such electrically charged fractions of molecules, the decomposition products of the molecules are attracted or repulsed by the plates (the so-called electrodes) through which the current is introduced. The negatively charged acid radicles make towards the positive entrance point of the electric current (the anode), whilst the positively charged metals seek the negative entrance point (the cathode). They there give up their respective charges, and thereby are separated, as will presently be described, as products of the decomposition of the dissolved substance. The passage of an electric current through a liquid is due to this movement of the fractions of molecule. Liquids, which do not contain decomposed molecules do not conduct an electric current unless they are fused metals. On account of this property of the decomposition products of the molecules of causing an electric current to pass through electrolyte solutions, they are named *ions* (derived from the Greek name for "wanderer"), and the positively charged metals streaming towards the cathode are termed *cations*, in contra-distinction to the negatively charged acid radicles or *anions* streaming towards the anode.

The ions present in the solution become converted, by having their electric charge withdrawn from them, into the uncharged atoms of elementary metals or uncharged acid radicles, which appear or are precipitated at the electrodes. They are thus different from the latter, as is shown by their whole behaviour. In a solution of common salt we have to assume that sodium ions and chlorine ions are present, in accordance with the theory outlined above, but we do not observe in such a solution any sign of the characteristics of elementary chlorine, which is a corrosive greenish gas, with an intensely pungent odour and bleaching properties; or of the characteristics of elementary metallic sodium, which decomposes water, with the formation of caustic soda (sodium hydroxide), and gaseous hydrogen, which escapes But if an electric current is passed into a solution of salt, there is a formation (particularly distinct) of chlorine gas at the anode, and sodium hydroxide and hydrogen at the cathode

Similarly, in the case of a solution of copper sulphate nothing can be seen of particles of "metallic" copper until the introduction of an electric current discharges the cupric ion and causes the copper to deposit as metal upon the cathode. The uncharged sulphate radicle formed by the discharging of the sulphate ion at the anode cannot exist as such, and therefore at the moment of its discharge it decomposes the water, with the formation of sulphuric acid and oxygen $SO_4 + H_2O = H_2SO_4 + O_2$

The electric charge is of the same strength in such aggregates of the molecular fractions as show correspondingly equal valencies (*i e* are equivalent). The quantity of a charge of electricity corresponding to a valency is termed an *electron*. Hence, in the electrolysis of sodium chloride there is invariably a simultaneous liberation of 23 grms of sodium and 35 46 grms of chlorine, in the process of discharging one sodium atom, the cathode throws off a negative electron, whilst in discharging one chlorine atom the anode takes up a negative electron

The difference in chemical behaviour between the ions and atoms (or atom groups) which correspond to them is expressed in formulæ by indicating each positive charge by , and each negative charge by ′. The ions are thus represented as individual substances distinct from the elementary atoms or uncharged acid radicles.

Thus we have metallic sodium, Na, the sodium ion Na·, elementary chlorine Cl, and the chlorine ion Cl′.

It is possible to regard the cations and anions as being already present even in the undecomposed, undissolved molecules, and their combination as being simply the result of the attraction of the particles containing different charges of electricity.

There would thus in the combination of two elements (*e.g.* sodium and chlorine) to form a salt be first a change from the elementary condition into that of ions containing different charges of electricity, and then a combination of these, through their reciprocal attraction, to form a molecule.

As a further development of this conception chemical affinity in general (reciprocal power of combination) may be represented as depending upon negative and positive charges. The individual elements have different electro-affinities, *i.e.* differ in their capacity of receiving an electric charge, and whereas many exert a strong attraction for a negative charge, others are characterised by being endowed with a slight positive charge. In the case of many elements both kinds of charge may be present, so that these elements have an *amphoteric* character, *i.e.* being positive towards negative substances and negative towards positive substances. For further particulars, see p. 62, Sec. 16.

The dissociation which takes place on the solution of an electrolyte, or the *ionisation* process, as it is also termed, is represented as a formula in the following manner: $NaCl \rightleftarrows Na^{\cdot} + Cl'$.

The complete ionisation of the sulphuric acid molecule corresponds to the formula $H_2SO_4 \rightleftarrows 2H^{\cdot} + SO_4''$ It may also undergo only partial decomposition: $H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4'$.

As was mentioned above, in the solution of the electrolyte there is a more or less pronounced dissociation into ions of the dissolving molecules, in addition to which molecules still undissociated are present in the solution.

The proportion of molecules decomposed into ions affords a measure of the extent to which this dissociation has taken place, and is termed the *degree of dissociation*. If, for example, out of 100 molecules 75 are decomposed into ions, the dissociation degree =0·75. If all the molecules are dissociated the dissociation degree is 1.

The greater the dilution of a solution, the larger is the proportion of molecules decomposed into ions, and in very dilute solutions practically all the molecules are dissociated. If the solutions are more concentrated there is an appreciable, and in many cases a large quantity of undissociated molecules present.

The dissociation capacity differs very much in the case of different substances. Thus strong acids, such as hydrochloric, nitric, and sulphuric acids, and strong bases, such as sodium or potassium hydroxide, are almost completely ionised in not very dilute solutions. The solutions of weak acids, such as *e.g.* acetic acid, contain, even when extremely diluted, many still undissociated molecules, whilst the base ammonium hydroxide, which as compared with potassium hydroxide is relatively weak, is dissociated to a much smaller extent than the latter (p. 25).

Just as an increase in the number of ions is associated with dilution, so, on the other hand, concentration of a solution (*e.g.* by evaporation of the solvent) is accompanied by a combination of ions. We have here, therefore, a reversible process, entirely analogous to that described on p. 12 *et seq.* Here, too, conditions of equilibrium must be established, for which in the case of acids and bases the law of mass action, described on p. 13, holds good in the same way as for other chemical reactions. Ostwald has shown that this also applies to more dilute solutions, and has expressed it as a formula in his so-called law of dilution. In such cases the following equation is applicable :—

$$\frac{[\text{Cation}].[\text{Anion}]}{[\text{Undissociated radicle}]}=K$$

where K is the dissociation constant of the substance in question. It is dependent on the temperature.

It was mentioned (p. 13) that the decomposition of ammonium chloride into hydrogen chloride and ammonia is checked when one of the substances formed as products of the decomposition is already present in the same space occupied by the gas, and similarly in this particular instance of the law of mass action the dissociation is influenced in an analogous manner. In the case of the simultaneous presence of two electrolytes with one ion in common the ionisation of each of these is less than if it alone were dissolved in the same volume of liquid. If, for example, ammonium acetate and formate are present together the total quantity of ammonium ion must be taken into consideration both for the equation

$$\frac{[NH_4^{\cdot}].HCOO']}{[HCOONH_4]}=K$$

and for the equation

$$\frac{[NH_4^{\cdot}].[CH_3COO']}{[CH_3COONH_4]}=K_1$$

Hence each of the salts is ionised to a less extent than if it were alone a solution.

If in the action of two solutions of electrolytes upon each other a reaction occurs, the process is one between the ions. If, for example, the action of hydrochloric acid upon silver nitrate is considered, the process which actually takes place is not that expressed by the equation: $AgNO_3+HCl=AgCl+HNO_3$, but since $AgNO_3$

is dissociated into $Ag^{\cdot}+NO_3{}'$ and HCl into $H^{\cdot}+Cl'$, the $Ag^{\cdot}+Cl'$ act upon each other in such a way that with the discharging of these ions silver chloride is precipitated; the solution will then contain $H^{\cdot}$ with $NO_3{}'$. As fast as the silver ions disappear a fresh portion of the residue of undissociated silver nitrate, which in the case of more dilute solutions is very small, is ionised, and the resulting silver ions again react with chlorine ions, until the whole of the silver or chlorine has been precipitated.

It will be seen that the same process must also take place when, instead of hydrochloric acid, sodium chloride acts upon silver nitrate, for, in that case, in addition to $Ag^{\cdot}+NO_3{}'$ there are present $Na^{\cdot}+Cl'$, and the ions $Ag^{\cdot}$ and Cl' react with one another in exactly the same way as in the previous instance. From this example it is obvious why in chemical reactions solutions of different salts of the same metal behave in the same manner, when it is a question of processes in which the *metal* (*i.e.* the cation) is concerned; and why, on the other hand, in those reactions in which the *acid* (*i.e.* the anion) is concerned it does not matter which salt of the acid effects the reaction. It is, in fact, only the ions and not the salts themselves which react.

Hence the processes which result in the formation of a precipitate are only apparently different, whether one writes, for example—

$$BaCl_2+H_2SO_4=BaSO_4+2HCl$$
$$\text{or } Ba(NO_3)_2+H_2SO_4=BaSO_4+2HNO_3$$
$$\text{or } BaCl_2+Na_2SO_4=BaSO_4+2NaCl, \text{ etc.}$$

The only process really concerned in the formation of the precipitate is: $Ba^{\cdot\cdot}+SO_4{}''=BaSO_4$.

If an element or an elementary group is present in *one* chemical compound in such a form that on dissociation it is liberated as an individual ion, but in *another* compound is in combination with other elements to form a group (or complex),[1] which on dissociation of the compound is liberated as an undivided ion, the solutions of these compounds will give entirely different reactions. For example, sulphides, with the ion S'', form precipitates with ferrous, cupric, and cobaltous salts, whereas sulphates, with the ion $SO_4{}''$, do not form them. Chromium in chromic salts is precipitated by ammonium hydroxide, in accordance with the equation: $Cr^{\cdot\cdot\cdot}+3OH'=Cr(OH)_3$; but if the chromium is present in the form of a chromate it is not precipitated by alkali hydroxides, for in that case it is contained in the anion CrO_4''.

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[1] See p. 10.

A distinct difference may be observed between reactions of the same element when present in two different forms of valency ($Hg_2^{\cdot\cdot}$ is precipitated, whilst $Hg^{\cdot\cdot}$ is not precipitated by Cl'); or between the reactions given by different groups of elements, which contain one element combined with other elements, in different proportions, *e g* ClO', ClO_3', ClO_4', or in which one element is in combination with different elements. Thus, for example, the two anions CN' and CO_3'', both containing carbon, differ in their behaviour, as do also the different acid radicles NO_3', ClO_3', CO_3'', SO_4'', etc , all of which contain oxygen, apart from the fact that they all act as acid radicles in a completely different manner.

An *acid* is characterised by containing *hydrogen ions*, a *base* by containing *hydroxyl ions*. The greater the extent to which the molecule of an acid or base is ionised, other conditions being equal, the stronger the acid or base.

The action of an acid or base consists in the fact that in a given reaction hydrogen ions (or hydroxyl ions) disappear, *e.g.* in the solution of zinc in acid $Zn+2H^{\cdot}\quad Zn''+H_2$, where it is a matter of indifference whether the anion is chlorine, sulphate ion, or any other.

In like manner the neutralisation of a base with an acid depends upon the combination of hydroxyl ions and hydrogen ions to form water: $HO'+H\quad -H_2O$, quite apart from the question of what cations and anions are also present.

The strength of an acid or base depends upon the acid radicle (anion) or metal (cation) which it contains. The greater the inclination of these substances to form ions, the more pronounced will be the degree of dissociation of the molecule in questions into ions.

This influence is therefore expressed in the dissociation capacity.

Strong acids or bases have great, and weak acids or bases slight dissociation capacity. The weaker an acid or base, the smaller is its dissociation constant.

Soluble *salts* have almost without exception a great dissociation capacity, and accordingly the more dilute solutions of salts are almost invariably ionised to a pronounced extent. They therefore reduce the dissociation capacity of acids with the same anion (or bases with the same cation, see p. 23) to an extent which increases with the decrease in the dissociation capacity (*i.e.* the strength) of the acid or base.

In this way, owing to the disappearance of hydrogen ions and the presence of undissociated acid molecules, the acid character of acetic acid is reduced to a minimum when sodium acetate is also present, of which fact especial use is frequently made in analytical chemistry. The addition of a salt of a weak acid to a strong acid has the effect of reducing its acid character, because the undissociated molecule of the weak acid takes the place of the hydrogen ions

$$(Na^{\cdot}+CH_3COO')+(H^{\cdot}+Cl')=(Na^{\cdot}+Cl')+CH_3COOH$$

Acid solutions, *i.e.* those containing hydrogen ions and characterised by a sour taste, are also described as solutions which contain "free" acid (and in an analogous manner alkaline solutions are said to contain "free" alkali). This mode of expression is a survival of the older mode of conception (p. 9, footnote), in which acids and bases in combination in salts were regarded as constituents of those salts in contra-distinction to free acids and bases.

In this connection it may be mentioned that the relative quantity of hydrogen ions[1] affords a measure of the strength, but not of the amount of free acid. The latter is equal to the sum of the dissociated and undissociated acid molecules.

If, for example, zinc is dissolved in acetic acid, the process, it is true, takes place only in accordance with the equation:

$$Zn+2H^{\cdot}=Zn^{\cdot\cdot}+H_2$$

(and indeed comparatively slowly since relatively few $H^{\cdot}$ ions are present), but the equilibrium

$$\frac{[H^{\cdot}].[CH_3COO']}{[CH_3COOH]}=K$$

is upset by the removal of $H^{\cdot}$ ions. In consequence of this new acetic acid molecules must continue to be decomposed until the equilibrium is again restored. If an excess of zinc is present this cannot take place, and the process continues until all acetic acid has been consumed.

In like manner it is possible to remove the hydrogen ions, as *e.g.* by the addition of sodium hydroxide solution (which contains hydroxyl ions to acetic acid. This produces water in accordance with the equation $H^{\cdot}+HO'=H_2O$, and a sodium acetate solution is formed, since the sodium and acetate ions remain in solution. If more sodium hydroxide is added than corresponds to the acetic acid present, there are no longer hydrogen ions to unite with all the hydroxyl ions, and the solution becomes alkaline. This process just described of the equalisation of the acid and alkaline characters of two solutions, *i.e.* the combination of all hydrogen ions (including those which are still in gradual process of formation) of one solution with all the hydroxyl ions of the other solution is *termed neutralisation*. The process can be followed with the aid of indicators (Sec. 17), blue litmus paper being turned red by acids, and red litmus paper blue by alkaline solutions. Solutions of neutral salts do not change the colour of either kind of litmus paper. This behaviour towards such indicators is also termed the "reaction" of the solution, which is said to have an acid, alkaline, or neutral reaction. For further details, see Sec. 17.

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[1] That is to say, the number which indicates what fraction of the hydrogen atoms replaceable by a metal is present in the condition of ions

The reaction described above of the combination of $H^{\cdot}$ and OH' ions must also, in accordance with the law outlined on p. 12, that fundamentally all the reactions are reversible, proceed (if only to a slight extent) in the direction of a decomposition of the water molecule into hydrogen and hydroxyl ions. It has in fact been proved that a very small amount of both ions is present in water.

This renders the relationships in the case of salt solutions still more complicated, for it is not only a question of the equilibrium —

$$\frac{[\text{Metal ion}].[\text{Acid radicle}]}{[\text{Salt}]} = K \quad . \quad . \quad . \quad (1)$$

in which for a solution in which no free acid or base is present [Metal ion] [acid radicle] invariably, but owing to the presence of the hydrogen and hydroxyl ions there are also the following conditions of equilibrium to be taken into consideration :—

$$\frac{[H^{\cdot}][OH']}{[H_2O]} = K(H_2O) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$\frac{[\text{Hydrogen ion}][\text{acid radicle}]}{[\text{acid}]} = K_1 \quad . \quad . \quad . \quad . \quad (3)$$

and

$$\frac{[\text{Hydroxyl ion}][\text{Metal ion}]}{[\text{Hydroxide}]} = K_2 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

If K_1 and K_2 are of approximately equal magnitude, the result when both are large (as when it is a question of the salt of a strong acid and a strong base) is that the tendency of the $H^{\cdot}$ or OH' ions in the water to combine with the acid radicle or metal ion to form undissociated acid or hydroxide is so slight, that neither $H^{\cdot}$ nor OH' ions are utilised to any appreciable extent; when both are small, an approximately equal quantity of $H^{\cdot}$ and OH' ions is used. In neither of these cases does any alteration of the reaction occur when the salt in question is added to the water? But if K_1 and K_2 are materially different, *i.e.* if the salt consists of an anion of a weak acid and a cation of a strongly basic character (or *vice versa*), the reaction is considerably influenced. The $H^{\cdot}$ ions originating from the water have, for example, a considerable tendency to unite with the anion of a weak acid, the acid radicle and the corresponding quantity of hydrogen ion disappear from the solution, and undissociated acid is produced (equation 3). Owing to the consumption of $H^{\cdot}$ ions the course of the equation 2 is such that it results in the formation in the solution of considerable quantities of hydroxyl as anions, which in accordance with equation 4 enter into equilibrium with the metal ions present. The solution becomes alkaline. In like manner, the solution of a salt which contains the anion of a strong acid associated with a weak basic cation will show an acid reaction.

Since this process may be regarded as a decomposition of the neutral salt by water into hydroxide and acid (the stronger portion of which is dissociated into ions, whilst the weaker remains practically undissociated) it is termed hydrolysis.

Apart from hydrolysis, there is also a certain degree of dissociation of the salt into its ions. Thus when aluminium chloride is dissolved in water it is dissociated, on the one hand, in accordance with the equation $AlCl_3 = Al^{\cdot\cdot\cdot} + 3Cl'$, whilst on the other hand, hydrolysis takes place in accordance with the equation

$$AlCl_3 + 3H_2O = Al(OH)_3 + 3Cl' + 3H^{\cdot}$$

In all cases in which the solution of a neutral salt, as defined on p. 7 (in which therefore acid radicle valencies correspond to all the valencies of the metal cations, and *vice versa*), shows an acid or alkaline reaction, hydrolysis has taken place. Thus the neutral (normal) Na_3PO_4 gives an alkaline reaction, and even the mono acid disodium hydrogen phosphate, HNa_2PO_4, is alkaline in its reaction, at all events towards litmus.

Separation from Solution.

The separation of a substance from a solution, *i.e.* the decomposition of a single phase into several, is the opposite process to its solution.

Such separation may be brought about in the first place by a change of temperature and pressure. This may cause, on the one hand, a dissolved substance to be transformed from a liquid into a gaseous or vaporous phase, so that a gas or a readily volatile substance escapes, while the solvent remains unaltered; on the other hand, cooling or partial evaporation of the solvent may increase the concentration above the saturation point, so that a solid substance separates in crystals, or the solvent may eventually completely evaporate and the dissolved substance be left as a solid residue All these transformations of the process of solution correspond to the simple, so called physical solution So far as they have a bearing on qualitative analysis they are described in connection with the methods of evaporation, distillation, and crystallisation The change into several phases may, however, be also associated with a chemical process which affects the dissolved substance, and causes portions of it to separate as a solid body or to escape as a gas: or it may be associated with a change of a solvent (*e g* the addition of alcohol to a pure aqueous solution) which causes the dissolved substance to separate unchanged In so far as these last two cases are concerned with the separation of solid substances, we speak of *precipitation*, which is described in Sec 5. For analytical chemistry this is of far greater importance than the separation of gases (Sec. 18) or of liquids from solution.

SEC 1.

2. Crystallisation.

Crystallisation in general is the change of a substance from the gaseous liquid (fused or dissolved) or even from the amorphous condition into that of crystals

Crystals are solid bodies with a regular uniform arrangement of the atoms throughout the whole substance

The result of this fixed juxtaposition of the smallest particles is not only a regular external limitation by flat surfaces, the edges and corners of which intersect at definite angles, but also a definite symmetry, characteristic of the substance in question in respect of all the properties which can be affected by a difference of direction (hardness, frangibility, elasticity, power of expansion when heated, heat conductivity, power of refracting light, etc)

Solids which in external form and symmetry of properties show none of the regularity characteristic of the substance are termed *amorphous* (formless). They correspond in all respects to fluids, but are distinguished from them by the fact that their inner friction is so great that the particles can no longer pass one another.

By crystallisation in the narrower sense is usually understood the preparation of crystals from solutions, by supersaturating a solution either by cooling or by evaporating part of the solvent (or by both simultaneously), and so causing separation in crystalline form. The more slowly the cooling and evaporation proceed, the slower is the growth of the crystals, but the larger and finer they are when formed.

Crystallisation does not inevitably occur when a saturated solution is cooled below its saturation temperature. Such solutions are termed sub-cooled or supersaturated. An external impulse, the most certain means being contact with a crystal of the dissolved substance, is required to start the separation of crystals.

For analytical purposes crystallisation by itself is of little importance, since, as a matter of fact, it never causes a complete separation of the substance in question from its solution, and so does not effect a quantitative separation of the substance from the solvent or from other substances in the solution.[1]

On the other hand, the properties of crystals, as shown both in their external form and, in particular, in their optical behaviour, which can be observed by means of a polarisation apparatus (or polarisation microscope) are capable of giving material assistance in the identification of substances. Crystallisation can also be used in the preparation of pure substances, *i.e.* in freeing them from impurities. For this purpose the substance is dissolved in the smallest possible quantity of water, and a new crystallisation promoted by cooling or evaporation. The impurities then remain dissolved in the residual liquid (the mother liquor). This method of recrystallisation is especially used for organic compounds, the process being repeated until on renewed recrystallisation the substance shows no further change in its properties (*e.g.* its melting point). The determination of the properties (*e.g.* the melting point, see Sec. 15) of such purified crystals may be used for the identification of the substance in question.

To obtain well-formed crystals from small quantities of liquid the solution is allowed to evaporate in the air, preferably, in the case of aqueous solutions, beneath a bell jar, under which there is also an open vessel half filled with strong sulphuric acid. A lens or a microscope is used for the more accurate observation of crystals. (See Sec. 23.)

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[1] It is of course possible to separate by crystallisation the bulk of substances which are present in very great quantity, and so to facilitate the detection of the substances still left in the residual solution (the mother liquor), as *e.g.* in the detection of small amounts of the alkali metals in sodium chloride solutions.

SEC. 5.

3. Precipitation.

The precipitation of a substance is its separation from a solution either *in consequence of an alteration of the solvent* (*e.g.* the separation of calcium sulphate from aqueous solution by the addition of alcohol) or, as is more frequently the case, as the *result of a chemical reaction in the solution*, whereby a new substance which dissolves with difficulty in the liquid is produced.

The substance which thus separates and usually sinks to the bottom is termed a *precipitate*.

Different kinds of chemical reactions may cause this effect. In far the largest number of cases they consist in a transformation of molecules caused by mixing two solutions, *i.e.* the ions previously n solution combine to form insoluble substances as, for example, $AgNO_3 + NaCl = AgCl + NaNO_3$, or $Ag^{\cdot} + Cl' = AgCl$. Whilst in this case sodium nitrate, or sodium and nitrate ions, remain in solution, here may also be cases in which (when the substances are present in solution in equivalent quantities) everything separates, as *e.g.* when olutions of barium sulphide and zinc sulphate interact, for the esulting compounds are then both insoluble

$$BaS + ZnSO_4 = BaSO_4 + ZnS$$

There is here a simultaneous completion of both ion reactions: $Ba^{\cdot\cdot} + SO_4'' = BaSO_4$ and $Zn^{\cdot\cdot} + S'' = ZnS$.

The precipitation reactions also include those in which a solid substance is dissolved, and another is precipitated in its place. If an iron rod is immersed in a solution of copper sulphate, copper separates and iron is dissolved: $Fe + CuSO_4 = Cu + FeSO_4$, or $Fe + Cu^{\cdot\cdot} = Fe^{\cdot\cdot} + Cu$.

The latter formula shows that it is here a question of the dis-harging of the cupric ion, since the iron originally present in elementary form replaces it in solution as a cation.

This property of iron is expressed by saying that iron has a greater *solution tension* (a greater solution pressure) than copper. The solution tensions for the change from the elementary to the ion ondition are characteristically different in the case of different metals, so that they can be arranged in an order of tension, in which one member invariably precipitates the following from their solutions. The precipitating metal is always more electropositive than the precipitated metal.

If an ion is not replaced by another, but anion and cation are simultaneously discharged, it is possible to precipitate the remainder of the ions deprived of their electric charge, provided that they are insoluble. This happens when an electric current is conducted into a corresponding solution. Thus copper is precipitated by an electric current, and owing to the withdrawal of its charge $Cu^{\cdot\cdot} + '' = Cu$.

Precipitations are also frequently brought about by the introduction of a gas into a liquid, as, for example, when lead sulphide is precipitated from a lead nitrate solution by means of hydrogen sulphide. $Pb(NO_3)_2 + H_2S = PbS + 2HNO_3$, or $Pb^{\cdot\cdot} + H_2S = PbS + 2H^{\cdot}$.

In contrast to the invariably gradual process of crystallisation, described in the previous section, the change which brings about the precipitation always takes place more or less suddenly, at all events in the case of the reciprocal action of two liquids mixed together, and the separation of the solid substance also as a rule takes place more or less rapidly. The process, however, is not always completed so rapidly, as to exclude the possibility of the formation of a regular grouping of the atoms, with the resulting production of crystals. The appearance of the precipitate therefore varies according to the conditions under which it is produced, and a distinction is drawn between crystalline, flocculent, pulverulent, caseous, and gelatinous precipitates. If the quantity of the new compound in process of formation exceeds by a not very considerable amount that contained in the liquid at the saturation point for the compound in question, only a supersaturated solution will at first be formed. In this case the separation of the precipitate is accelerated by shaking and by rubbing the sides of the vessel with a glass rod.

If the precipitation takes place rapidly, the substance frequently separates first in an amorphous condition, and then under certain conditions subsequently becomes crystalline on standing

The form of the precipitate depends, on the one hand, upon the concentration and temperature of the solution, *i.e.* upon the interacting solutions, and, on the other hand, upon the nature of the separating substance. It is, therefore, frequently possible to draw a conclusion concerning the separated substance from the appearance of the precipitate, its form and colour. Precipitation may thus be used for the identification of substances, and in such cases is of value even when a complete separation of the substance in question does not occur.

A much more frequent use of precipitation, however, is to separate substances from one another, by converting one or more of several substances in solution together into a precipitate whilst others remain in solution, so that then a mechanical separation of solid and dissolved substances may be effected. To attain this end the precipitation must be as complete as possible.

The only substances suitable for this purpose, therefore, are such as are soluble with difficulty (practically insoluble), and the conditions affecting the liquid from which precipitation is to be made must be so adjusted that the relative insolubility is increased as much as possible. For this reason as small a volume of the liquid as possible is taken (especially in the case of substances which are sparingly soluble), and the temperature of the solution is, in most cases, kept low. The solubility of a substance in a liquid may also be reduced by altering the solvent, *e g* by the addition of alcohol to an aqueous solution of calcium sulphate. Moreover, experience has hown that in the case of the actual precipitation reactions the relative insolubility of the precipitate is increased when one of the two interacting substances is present in excess. Thus barium sulphate is considerably more soluble in pure water than in water which still contains in solution either sulphate ion or barium ion. Since, herefore, barium sulphate is always precipitated for the purpose of separating either the barium or the sulphate ion from solution, an excess of sulphate is used in the first and of barium in the second case.

This old empirical practice has its explanation in mass action, *e.* in the conditions of equilibrium between the ions and the undissociated part of the substance.

As was explained on p. 23, the condition under which equilibrium s attained in solutions of salts is that the product of $[\text{Anion}] \times [\text{Cation}]$ $K \times$[undissociated salt]. The concentration of the undissociated substance must be constant in a solution which is in contact with undissolved portions of the said substance, *i e.* saturated with it and in cases suitable for analytical precipitations must be very mall). Hence the product $[\text{Cation}] \times [\text{Anion}]$ the so-called *solubility product*[1]—is also constant. In proportion, then, as one factor of this product increases in the solution (through the addition of xcess of precipitant), the other factor must become smaller, and more complete separation of the ion in question be thereby attained. This influence of an excess of one of the two ions becomes more ecisive with the increase in solubility of the original substance, so that in cases where precipitates which are relatively soluble are formed, a correspondingly large excess must be added to produce a precipitation, which, however, may then under certain conditions be nearly complete. The sulphate ion, for example, can be almost quantitatively precipitated as benzidine sulphate (notwithstanding the fact that the latter is by no means insoluble), provided that an excess of about 50 per cent. of the precipitant is used.

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[1] If the precipitate has the formula $\text{Cation}_n . \text{Anion}_m$, as *e g.* $Ca_3(PO_4)_2$, he solubility product must correspond to the general form of the law of mass ction: $[\text{Cation}^n] . [\text{Anion}^m]$, as *e g.* $[Ca^3] . [PO_4^2]$.

Sometimes a precipitate may also redissolve in excess of the precipitant, owing to a new chemical reaction taking place between the two (*e.g.* formation of a complex, p. 10).

In this way, too, the presence of a third substance, although not contributing to the primary reaction, may influence the final result by entering into a further reaction with one or other of the interacting substances, or with the precipitate produced by them.

Thus, for example, the addition of an ammonium salt influences or inhibits the precipitation of magnesium hydroxide by ammonia from the solution of a magnesium salt.

The occurence of a precipitate in the reaction

$$MgCl_2+2NH_4OH=Mg(OH)_2+2NH_4Cl \quad \text{or} \quad Mg^{\cdot\cdot}+2OH'=Mg(OH)_2$$

depends upon the fact that so many $Mg^{\cdot\cdot}$ and OH' ions are simultaneously present in the solution, that the solubility product $[Mg^{\cdot\cdot}].[OH']_2$ is exceeded.

The presence of an ammonium salt, however, checks the dissociation of the ammonium hydroxide, and thus reduces the concentration in OH' ions, with the result that more $Mg^{\cdot\cdot}$ ions can remain in solution, and the precipitation thus becomes less complete or does not take place at all. Since, under any conditions, in the precipitation of a magnesium salt with ammonia ammonium ions are added to the liquid, only a part of the magnesium can be precipitated as hydroxide.

In like manner the presence of *e.g.* hydrogen ions prevents the separation of precipitates of weak acids, by checking their dissociation to such an extent that the solubility product is no longer reached.

Thus potassium chromate in acid solution does not precipitate, *e.g.* strontium, *i.e.* precipitated strontium chromate, is soluble in acids, for $(2K^{\cdot}+CrO'_4)+(2H^{\cdot}+2Cl')=(2K^{\cdot}+2Cl')+H_2CrO_4$. In this case the chromate ions are withdrawn. Should this take place to any considerable extent the solubility product $[Sr^{\cdot\cdot}].[CrO''_4]$ is no longer reached, and no precipitate can be produced (see also Sec. 101).

Even in cases where a direct repression of the dissociation of the precipitant (through the presence of an ion of the same character in the solution) cannot be assumed, but in which the completeness of the precipitation is influenced by the presence of a third substance (*e.g.* the precipitation of barium sulphate by salts of potassium, sodium, calcium, or magnesium, or of calcium carbonate by the salts of alkali metals, etc.), it is necessary to assume that the substance in question enters into a by-reaction with one of the substances taking part in the precipitation reaction, or with the substance to be precipitated (to form a double salt, complex or the like), so that the entire quantities of the substances present are not available for the equilibrium equation $[K^{\cdot}].[A']=K$.

Since the object of precipitation is the separation of the substances thrown out of solution, it is essential for the subsidiary processes of decantation and filtration, described in the following sections, that the precipitate shall *not be too fine*. Otherwise it remains suspended in the liquid, and passes through the pores of the filter (Sec. 6). In many cases this may be obviated by shaking, and especially by allowing the precipitate to stand in a warm place. In the former case there is a formation of *larger flocks* through the coalescence of the smallest particles which attract each other, and in the latter there is *an increase in the crystalline nucleus* of the precipitate. This is due to the fact that the solubility of a substance in a liquid depends upon the relative area of its surface, and that the greater this area (*i.e.* the smaller its particles) the greater surface tension does it possess. Hence when larger and smaller crystals of the substance are in contact with the solution, it is possible for the latter to be saturated as regards the larger crystals, but not completely as regards the smaller crystals. The result of this is that the very small particles dissolve, whilst the larger ones increase in size. This process only takes place to a notable extent in the case of very small crystals, which have a large surface in proportion to their size.

Separation in the *colloidal* condition is a form of separation, which under certain conditions occurs in precipitation reactions, without the formation of a true precipitate, and represents a still finer state of distribution of the solid substance in the liquid than the finest precipitate (see Sec. 9). Substances in this form of distribution do not subside, and cannot be separated by filtration. It is frequently possible, however, to cause such colloidal substances to separate in the form of ordinary precipitates by introducing an electrolyte into the solution. Thus, for example, hydrogen sulphide does not produce a true precipitate in an aqueous solution of arsenious acid, but causes the formation of arsenic trisulphide in colloidal form. The liquid turns yellow, but remains clear. But if hydrochloric acid is then added, a flocculent precipitate is formed. A similar behaviour is shown by cupric ferrocyanide, which in pure water remains distributed in colloidal form, whilst in the presence of a salt it forms a precipitate. As a general rule, it is often possible to cause precipitates in a very fine state of division to separate in a flocculent form by the addition of salts, so that they can be separated from the liquid.

It is also frequently possible by applying heat to cause colloidal substances to separate. Silicic acid when liberated from silicates is always obtained in a colloidal form, in which it cannot be separated from the liquid, so that it remains partly in (apparent) solution.

Separation of Precipitate from Liquid.

Two different processes are used in analysis, according to the conditions, for the separation of a liquid from a solid substance which is present in it, viz. *filtration and decantation*. Both are supplemented by *washing*.

SEC. 6.

4. Filtration.

In this operation the object mentioned above is attained by pouring the liquid, together with the particles contained in it, from which it is to be separated, on to a fine porous medium, as a rule on to unsized paper (filter paper, placed in a funnel), as this allows the liquid to drain through, whilst the solid particles are retained.

The liquid which runs through is termed the filtrate, and the solid particles remaining on the filter paper the (filtration) residue.

In order that the retention of the precipitate may be complete and the filtration rapid (because finely divided gelatinous precipitates choke the filter pores), care should be taken that the precipitate is as granular or flocculent as possible, and it is therefore advisable to allow the precipitate to stand for sufficient time (see p. 35), so as to cause the colloidal precipitate to coagulate (see pp. 35 and 44).

In the case of very fine precipitates which can easily pass through the filter paper, clear filtrates can often be obtained by placing one filter paper within another. In similar cases a clear filtrate can often be obtained by mixing filter-paper pulp with the liquid.

Occasionally a precipitate passes through the filter paper at the beginning of filtration, but after a while particles of the precipitate fill up the filter pores, and thus form a more compact filtering medium, so that a clear filtrate is obtained. The first turbid filtrate is repeatedly poured over the filter, and this results in a quite clear liquid. It is occasionally necessary to repeat this process several times before the filtrate is clear.

Warm liquids can be filtered more quickly than cold ones. It is, therefore, preferable to filter the solutions while hot.

With a few exceptions, the *funnel* should be of glass (Sec. 24, 8) The sides should be smooth and at an angle of 60°, so that the filter paper can lie evenly against them. Funnels with a long comparatively narrow outlet tube[1] are most suitable for rapid filtration. It is advisable to fix them in a *filter stand,* so that they keep in a rigid position.

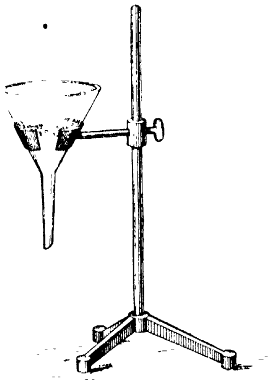

Fig. 1.

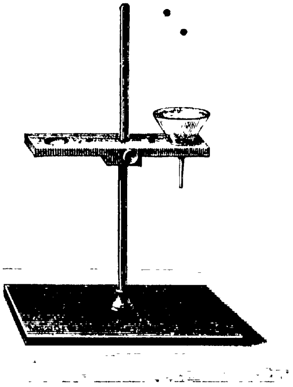

Fig. 2

Figs. 1 and 2 show suitable kinds of filter stands. Wooden ones have the advantage that the acid vapours of the laboratory air do not affect them, but in time the base is apt to be attacked by alkaline or acid liquids unavoidably dropping on to it, so that the receptacles for the filtrate no longer stand evenly on it. In addition, wooden stands may warp. Iron stands are steadier, but rust easily, and therefore there is the danger of particles of rust from the upper part falling into the liquid undergoing filtration, and either mixing with the precipitate or contaminating the filtrate by dissolving in it.

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[1] *Zeitsch. anal. Chem.*, **44**, 117.

This can to a certain extent be avoided by covering the stand with bituminous varnish, but this coating of varnish renders the adjustment at different heights of the clamp holding the funnels rather more difficult. Brass rods are more resistant to the action of acid vapours, but if they are attacked obviously involve the risk of contaminating the filtrate or precipitate by copper or zinc compounds. *Ostwald*[1] recommends the use of a ring open at one side, into which the tube of the funnel can be inserted sideways. This is handier and lessens the risk of liquid dropping on to the stand. In iron stands the ring is generally lined with porcelain or cork.

The *filter papers* are generally used *smooth*, but sometimes *fluted*. The former are chosen when the solid substance to be separated is required for subsequent use, and the latter (which render a more rapid filtration possible) when it is only a question of obtaining a clear filtrate. Smooth filter papers which are placed in the funnel in such a way that they lie flat against the sides, are obtained by folding a circular piece of paper twice in such manner that the folds are at right angles. As, however, this means that one side of the paper consists of three thicknesses, so-called open filter papers, as shown in Fig. 3, are recommended for many purposes. (They can be bought ready cut.) Here *a* is folded over *b*, and the projecting part *c* is wrapped over *a*.[2] It is easier to demonstrate than to describe the preparation of fluted filter papers, which can be made in various ways and can also be bought ready made. If the contents of the filter paper have to be washed, the paper should not project beyond the edge of the funnel, but should always be at least ½ cm. below it. In most cases it is advisable to moisten the smooth filter papers before use (and to insert them in such a way that the outlet tube of the funnel remains full of liquid), because not only can the filtration be carried out more quickly, but the substances to be filtered do not pass through the pores so easily. *Paper* which is chosen for filtration purposes should be as free as possible from inorganic substances, especially those which are dissolved by acids (iron or calcium compounds). Bought filter papers seldom comply with these strict

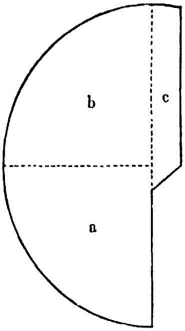

FIG. 3.

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[1] *Zeitsch. anal. Chem.*, **31**, **182**.

[2] *Ibid.*, **36**, **506**.

requirements, and for *delicate analysis* it is essential that the filter papers be washed with acid and water. Papers washed with hydrofluoric acid and hydrochloric acid as well as the unwashed ones can be purchased ready for use. If it is desired to wash the papers personally, the apparatus shown in Fig. 4 should be used for the purpose. *A* is a flask with no bottom, containing two sheets of glass *a* and *b*, between which the ready cut and folded filter papers are placed. A short glass tube *d* is fitted into the cork *c*, and has a small rubber tube *e* attached to it, which is closed at the bottom by means of a small glass rod or spring clip. The flask is filled to above *a* with a mixture of one part of hydrochloric acid of 1·12 sp. gr. and two parts of water, and allowed to stand for 4–8 hours.[1] The acid is then allowed to run off by opening the clip on *e*. After closing the opening again, the flask is filled with clear well or tap water, which is allowed to stand for an hour before being run off, and the washing with such water is repeated until the last washings show no acid reaction; the washing is continued with distilled water until a sample of the liquid draining off, mixed with a few drops of a solution of silver nitrate, no longer gives a turbidity. After washing, the papers are placed between layers of blotting-paper and dried on a porous medium at a gentle heat. If only a few filter papers are to be washed, they should be laid within one another, as for filtration, in a funnel, sprinkled with moderately dilute hydrochloric acid or nitric acid, and after a while thoroughly washed with tap water and finally with

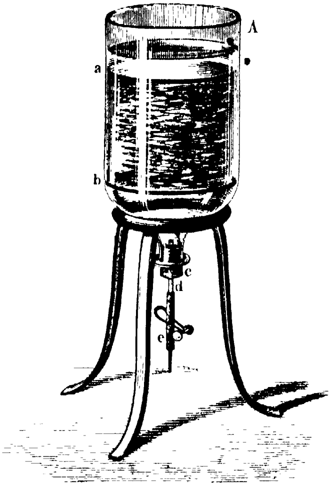

FIG. 4.

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[1] Filter papers easily become brittle if too strong acid is used, or if they are allowed to remain too long in contact with the acid.

distilled water. Apart from its purity, the character of a good filter paper depends on the speed with which liquid can pass through it, and the manner in which it retains suspended precipitates, even finely divided ones such as barium sulphate, calcium oxalate, etc. If paper cannot be obtained which fulfils both requirements it is advisable to keep a supply of two kinds, a thick quality for the separation of very fine precipitates, and a more porous one for the purpose of a quick filtration of coarser particles. For some time it has been possible to obtain filter papers hardened by treatment with nitric acid, which, owing to their firmness, are excellent for filtration and are but little attacked by alkaline hydroxide and acids.

Filtration with the aid of a suction apparatus is described in the introduction to quantitative analysis.

With regard to the many suggestions for *automatic filtering apparatus* with a continuous or intermittent washing of precipitates, reference should be made to the *Zeitschrift für analytische Chemie*.

SEC. 7.

5. Decantation or Pouring off.

This operation is often used instead of filtration, when the solid particles are of considerably greater specific gravity than the liquid from which they are to be separated. They then subside more rapidly and form a deposit, so that the supernatant liquid can be either poured off by tilting the vessel or drawn off by means of a siphon or pipette. In many cases decantation must be used instead of filtration in order to free precipitates completely from the liquids in which they are contained, especially when a precipitate is so gelatinous that it rapidly chokes the pores of the filter paper when laid on it; as a matter of fact, in this case complete washing of the precipitate upon the filter would be impossible. Occasionally decantation and filtration are combined by leaving the precipitate as far as possible in the vessel in which it has subsided, but pouring the liquid through a filter in order to render it completely clear.

SEC. 8.

6. Washing.

If the object of filtration or decantation is to obtain a solid substance in a pure condition, that is to say its complete separation from the solution from which it was precipitated, it must be freed from the liquid adhering to it by repeated washing. This operation is termed *washing*. Washing by decantation consists simply in stirring the precipitate with water or other fluid after the liquid has been poured off, allowing it to settle, pouring it off again, and so on. For washing a precipitate collected on a filter a washing bottle is used (Fig. 5).

The illustration needs no explanation. The tube pointing to the left is drawn out to a fine open point. If it is desired to make this tube movable, the shorter arm of the tubes should be cut through and the two parts connected together with rubber tubing. By blowing into the upper tube a fine jet of water is forcibly driven out of the lower one; this is especially suitable for washing precipitates Washing-bottles of this description have the advantage that they can be used for washing with hot water. In order to hold the bottle when filled with hot water, the neck should be surrounded with cork or felt and this made firm by binding it with cord, or it can be bound, as shown in the illustration, with several lengths of cord only.

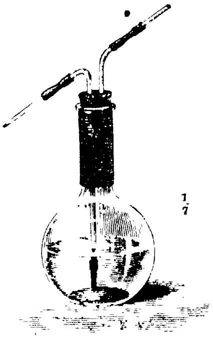

Fig. 5.

As the success of an analytical operation often depends on the proper washing of the precipitates, care should be taken that all parts of the precipitate are brought uniformly into contact with the washing liquid, and that the edge of the filter paper not covered by precipitate is also washed.

By observing the following rules the complete washing of a precipitate on the filter may be accelerated, and at the same time the quantity of washing liquid required will be reduced to a minimum; only add fresh washing liquid to the filter when the former quantity has completely run off, and always fill the filter up to the upper edge of the paper. The precipitate should be broken up with the jet of water coming from the washing-bottle, provided, of course, that there is no risk of the filtrate becoming turbid.

In the case of gelatinous precipitates the washing liquid often runs through so slowly that they cannot be washed on the filter. In such cases the precipitate is forced from the filter paper by means of the jet into a beaker or dish, is washed there by decantation, and only then placed on a filter paper again.

Washing should be continued until its object has been actually attained. This is, as a rule, only the case when the precipitate has been *completely* freed from the adhering liquid.

Guesswork must not be relied on, and as a proof, a suitable test must be applied to the last washings run off. If the substance to be removed by washing is solid and not volatile, it will generally suffice if a drop of the washing liquid is slowly evaporated on a strip of platinum foil; if it disappears entirely the object of the washing has been attained. In many cases a test applied to the final washings with a test paper or suitable reagent (silver nitrate) (p. 65) will prove whether a precipitate has been thoroughly washed.

Another method which has been suggested of determining whether the washing of a precipitate is complete is to draw a deduction from the amount of washing liquid used. Presuming that every time washing liquid is poured over the precipitate, the fluid still adhering to the precipitate is diluted to a certain extent, it is easy to reckon, taking into consideration the number of times washing has taken place, how large a proportion of the original filtrate can remain in the precipitate. It has been proposed, for example, that washing continued until the dilution is ten thousandfold is invariably sufficient. This does not, however, meet all cases, because the substances to be separated are not only present in dissolved form between the particles of the precipitates, but also, according to the nature of the precipitate, adhere to its surface in varying quantities owing to adsorption, so that they cannot be as readily washed as the calculation shows. *A direct test is safer and therefore always to be recommended.*

The size of the granules in the precipitate is of importance both as regards the quantity of the liquid enclosed between the particles of the precipitate, and also as regards the quantity of substance which the surface adsorbs (see p. 35), and washing is easier the more coarsely granular are the precipitates.

When the solubility of the precipitates in the liquid from which they are separated is materially different from their solubility in water or the washing liquid, or when the precipitate changes into the colloidal suspension (p. 35 and Sec. 3) after removal of the solution, the filtrate will become turbid if it is mixed with the washing water.

If there is the risk of this occurring it is advisable to collect the washing water separately in order to obtain a clear filtrate.

In order to avoid the possibility in such cases of a portion of the separated precipitate being washed away in this manner, suitable substances must be added to the washing water (*e.g.* ammonia for the washing of magnesium ammonium phosphate or a salt for the washing of colloidal precipitates).

Where possible it is advisable to wash with a hot liquid, both with the object of obtaining more rapid filtration and for more complete solution of the adsorbed substances.

Liquids which do not mix with water will not flow through a filter paper moistened with water, and one can therefore separate them from aqueous solutions by this method, *e.g.* carbon bisulphide or a solution of iodine in carbon bisulphide.

Separation of Dissolved Substances from one another.

For the separation of substances present in solution or in pseudo-solution processes can also be used in which the substances remain in the dissolved condition, but in which they are obtained in separate solutions. Processes which produce this result are *dialysis* and *shaking* or *extraction*.

SEC. 9.

7. Dialysis.

The *colloidal condition* is, as was mentioned on p. 35, an intermediate stage between true solution and the finest suspension, *i.e.* there is still no visible heterogeneity present, but the particles of the colloidal substance are regularly distributed throughout the liquid as in the case of a true solution. But compared with the ordinary molecules or ions they are relatively large, so that although they are not directly visible, yet they reflect, refract (or bend) light, and by this produce certain optical effects, in consequence of which colloidal solutions appear coloured or turbid (opalescent).

It is not possible, however, to draw a sharp distinction between the finest suspension or emulsion and colloidal solution on the one hand, or between the latter and a true solution on the other. But in practice it is possible to fix the limits for the colloidal condition by the fact that the individual particles regularly distributed throughout the liquid vary in size from a 10,000th part of a millimeter ($0{\cdot}1\mu$) and a millionth part of a millimeter ($1\mu\mu$).

Particles which are greater are retained by the paper filter and are still visible under the microscope, but smaller particles approximate to molecules in size and are distinguished from colloids by their power of diffusion described below.

A colloidal distribution of a substance in a liquid (pseudo-solution) is called "sol" in contra-distinction to the substance "gel" separated from such distribution by coagulation.

It was mentioned on p. 35 that such a precipitation is in many cases caused by the addition of electrolytes. This process usually depends on the fact that the colloids are electrically charged (more frequently negatively than positively). When they encounter ions oppositely charged they are discharged and thereby precipitated. It has been found that the higher the valency of the ions, *i.e.* the more electrons to which their charge corresponds the greater is their activity in this respect.

Two oppositely charged colloids can also reciprocally discharge each other and be precipitated.

In the case of many colloids there is a combination of the substance distributed through the liquid with the molecules of the latter (usually water) to form larger complexes, which on their part, in contra-distinction to the behaviour of a true liquid, are distributed between molecules of the substance. In such cases the precipitating action of many salts is due to the fact that it has a dehydrating action on these complexes.

There is an essential difference between true solutions and colloidal "pseudo-solutions" with regard to their diffusion capacity, *i.e.* their *power of penetrating into another layer of liquid* with which their fluid particles can mix uniformly. In the case of true solutions the dissolved substance spreads uniformly into the solvent in accordance with the same laws as does a gas into an empty space, *i.e.* one containing another gas. If such a solution is covered with a pure solvent, mutual mingling takes place (so-called diffusion) until uniform mixture is obtained. The dissolved substance is distributed through the liquid in consequence of its *osmotic pressure* (the reciprocal power of attraction between it and the solvent).

Colloidal substances diffuse either not at all or only to a very slight extent into liquids. Here, too, there is a gradual transition, since simultaneously with the growth in the size of the particles, there is an increase in the forces which counteract the tendency towards a homogeneous distribution in the liquid. (Friction, separation due to specific gravity, reciprocal attraction of homogeneous masses, etc.)

The difference is shown still more clearly in the case of diffusion through *porous diaphragms*, such as the membrane of an animal bladder, parchment paper, etc., than in free diffusion. Such "porous" diaphragms have such fine openings that liquids can penetrate into them, but contrary to what happens in the case of filter papers, do not pass through them into the air, but can only evaporate. If, however, such a porous membrane is interposed between two liquids which can moisten it, both of these liquids penetrate to the other side of the molecule and back again, so that a reciprocal flow takes place in both directions, although with a different velocity.[1]

In the case of true solutions the molecules of the dissolved substance pass, together with those of the solvent, through the dividing membrane, whereas the large particles of a substance distributed in colloidal form through the liquid cannot penetrate through the fine openings of the membrane, but remain on one side of it.[2]

This difference was first observed by Graham, who used it as a means of separating substances in colloidal solution from those in true solution, and termed the method "*dialysis*."

Since substances present in true solution are obtained as crystals on evaporating the solvent, Graham termed the substances passing through a porous membrane *crystalloids*, to distinguish them from the *colloids* left behind.

The *primary* distinction drawn by Graham between particular substances cannot be maintained in its entirety, since, as a matter of fact, *all* substances can be disintegrated into the colloidal condition In practice, however, it is possible to distinguish between the substances which readily form true solutions, and those which almost invariably form only colloidal pseudo-solution. For the separation of these two kinds of substances dialysis is an exceedingly useful method.

Crystalloids in this sense include, *e.g.* sugar, salts, and alkaloids;

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[1] Thus pure water diffuses more rapidly into salt solution than *vice versa*.

[2] Just as, speaking broadly, there is no sharp distinction between fine suspension, colloidal condition, and true solution, so too the same remark applies to the retention of such substances by porous media. Filter papers retain true precipitates, very thick papers keep back very fine suspensions, whilst porous membranes will prevent the passage of colloids (which pass through a filter) but allow substances really in solution to pass. But even these last may be kept back by certain (semi-porous) membranes, which are still permeable by solvents. Semi-porous membranes of this type are formed, *e.g.* by the membranous precipitates of cupric ferrocyanide. Owing to such a dividing film between a solution of sugar and pure water, the latter can penetrate into the sugar solution, which, however, cannot diffuse into the water. If the liquids were originally at the same level on both sides of a dividing membrane, a difference of level (*i e.* of pressure) results. The process continues until the excess of pressure on the side of the sugar solution is equal to the *osmotic pressure* of the latter, *i e.* until the equilibrium is reached between the attraction of the sugar for the water (which causes a dilution of the sugar solution) and the excess of pressure which opposes the influx of the water.

whilst examples of colloids are, *e.g.* glue, india-rubber, dextrin, enamel, tannin, albumin, extractive substances, silicic acid, etc. A suitable apparatus for dialysis is that shown in Figs. 6 and 7. In Fig. 6 the liquid to be dialysed is placed in the open bell-shaped glass vessel, over the bottom of which a parchment paper has been tied, whilst in Fig. 7 it is introduced into the ring, the bottom of which is also composed of parchment paper. This ring is made of wood, or better, of gutta-percha. The diameter of the parchment paper with which the bell or ring is covered must exceed that of the bell or ring by about 10 cm.; it is moistened when drawn over the opening and secured by string or elastic bands, but must not be stretched absolutely tightly. The parchment paper must be free from any places which would allow liquid to pass when moistened on one side only; this is tested by placing pure water on the upper surface and observing whether moist spots appear on the underside. If faults are found they must be remedied by applying liquid albumin, coagulating it by heat. When the dialyser has been proved to be trustworthy it is charged with the material under examination. If the latter is quite fluid, the bell apparatus may be used, but if it

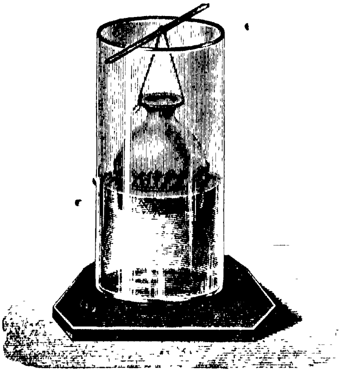

FIG. 6.

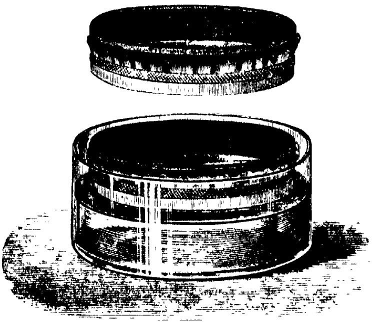

FIG. 7.

also contains solid substance the ring apparatus is preferable. Care must be taken that the height of the liquid in the dialyser does not exceed 1·5 cm., and then the membrane should be slightly immersed in the water in the outer vessel, the quantity of which should be at least four times as great as that of the liquid to be dialysed. For this purpose the bell is suspended in a suitable manner, as shown in the figure, whilst the ring is simply allowed to float on the water. After 24 hours half to three-quarters of the crystalloid substances will have passed into the outer water, whilst the colloidal substances have remained in the dialyser; only traces, at most, of the colloids will have simultaneously diffused into the exterior liquid. By repeatedly bringing the dialyser into contact with fresh quantities of water it is possible eventually to separate the whole of the crystalloid substances from the colloidal substances. When only the colloidal portion is required the use of parchment thimbles (which can be purchased) is a very rapid method of effecting the separation. The liquid is introduced into this capsule, which is then suspended in a vessel through which flows a constant stream of water. Dialysis may frequently be of great use in forensic chemical investigations (see Sec. 201).

SEC. 10.

8. Extraction by Shaking and Continuous Extraction.

In order to separate several substances which are in solution together, or to extract a dissolved substance from its solution, a process may be used in which the solution is intermingled with other solvents, in which it is insoluble or only sparingly soluble, but which has a greater solvent action than the first solvent upon the substance. When the mixture of the two solvents which have been brought into intimate contact, usually by shaking, is allowed to stand, it separates into two layers, which can be separated from one another. In practice this is usually effected by means of a separating funnel, Fig. 8.

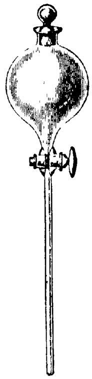
FIG. 8.

As a rule a relatively readily volatile solvent is used for the "shaking out" process, so that when it is evaporated the substance extracted from the first solution may be obtained.

The extraction of the substance in question from the first solution is usually incomplete, but as the result of the shaking there is produced a condition of equilibrium in the sense that the concentration of the substance to be extracted from the first solvent stands towards its concentration in the second solution in a relationship which is a constant for the substance in question and the two solvents. This constant is termed the *distribution coefficient*, and under normal conditions is equal to the ratio of the solubilities of the two substances in the respective solvents. If, for example, a single shaking of an aqueous solution with a definite amount of ether transfers $\frac{3}{4}$ of a substance into the ethereal solution, a second shaking of the separated aqueous layer with the same quantity of ether will again remove $\frac{3}{4}$ of the substance remaining in solution, leaving still $\frac{1}{16}$ dissolved in the water; whilst a third shaking will then leave only $\frac{1}{64}$ of the original substance behind. In this way it is possible, as in the case of washing, to reach a point where the residue is practically equal to *nil*.

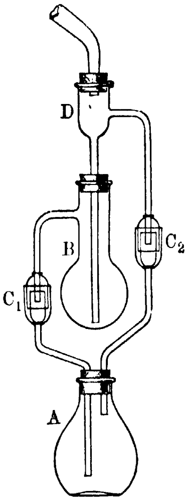

FIG. 9.

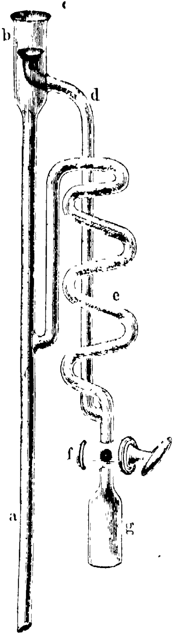

FIG. 10.

In cases where the distribution coefficient is unfavourable the result may only be attained by long-continued repetition of the process. In some cases, therefore, it is advisable to use a process of *continuous extraction* instead of shaking.

An extraction apparatus for liquids devised by H. Schwartz[1] is shown in Fig. 9. The solvent is heated to the boiling point in the

[1] *Zeitsch. anal. Chem.*, **23**, 368.

boiling flask A. The vapours are conducted through the tube, the lower end of which terminates just below the cork, into D, whence they pass into a reflux condenser (only the lower end of which is shown in the figure), and the condensed liquid falls back into D. From the lower end of the thistle funnel D it is delivered into the flask B containing the liquid to be extracted, rises drop by drop to the surface and, charged with the extracted substance, flows back into A through the side tubulure in the neck of B. C_1 and C_2 are mercury seals.

Fig. 10 represents a universal extraction apparatus devised by Gadamer.[1] The tube *a* is connected with the boiling flask, whilst the reflux condenser is attached to the tube at *b*. The condensed liquid falls through *c* and *d* to the lower end of the spiral tube *e* containing the liquid to be extracted, through which it percolates in a long column. At the beginning of the extraction the tap *f* is closed, and mercury introduced through *c* until it reaches the opening from *d* into *e*, so raising the level of the liquid to be extracted above this opening. If solvents are to be used which are heavier than the liquid to be extracted (*e.g.* chloroform) the apparatus is reversed, *a* closed with a stopper, *b* connected with the boiling flask, and *g* with the condenser. For details of the construction of other types of extraction apparatus reference may be made to the sections on the subject in the *Zeitschrift für analytische Chemie*, *e.g.* **41**, 691 *et seq.* Partheil's apparatus, for example, is particularly effective.[2]

It is unnecessary to deal more fully here with the extraction of solid substances, which is of importance in quantitative analysis. It is described in the introduction to quantitative analysis.

Separation of Volatile from Non-volatile Substances.

The processes used for the separation of volatile substances from those which are non-volatile or only slightly volatile are *evaporation*, *distillation*, *ignition*, and *sublimation*. The first two are always concerned with liquids, and the others with solid substances.

SEC. 11.

9. Evaporation.

This process is one of those most frequently used in analytical chemistry.

It is invariably chosen when it is desired to evaporate completely or partially a volatile liquid, the escaping vapour from which it is not of importance to recover.

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[1] *Archiv. d. Pharm.*, **237**, 68; *Zeitsch. anal. Chem.*, **41**, 693.

[2] *Zeitsch. Untersuch. Nahr. Genussm.*, **5**, 1049; *Zeitsch. anal. Chem.*, **42**, 127.

For example, liquids, such as the washings from a precipitate, are evaporated to ascertain whether they contain in solution soluble non-volatile substances; or the solvent is completely expelled from solutions, when it is a question of obtaining the dissolved substances[1] in solid or liquid form; or only a part of the solvent is evaporated when the concentration of a solution is required (*e.g.* for the crystallisation of a dissolved substance).

It is also a common practice to remove volatile substances (*e.g.* carbon dioxide, ammonia, hydrogen chloride) from aqueous solutions, by the simultaneous evaporation of part of the water (which is subsequently replaced when it is desired to keep the concentration the same in other respects).

Evaporation consists, as its name indicates, in the conversion of the liquid into vapour. In the majority of cases this is effected by heating, either to boiling point or even to a temperature below the boiling point.

Exposure to the air or in a closed vessel from which the vapours are continually removed (*e.g.* by suction or by absorbent substances) may also be used for evaporating liquids. Even if heat is not used for the purpose the process is known as evaporation. Agents used for the absorption of the vapour formed on evaporating aqueous solutions include concentrated sulphuric acid, calcium chloride, phosphorus pentoxide, etc.

Evaporation by heat is usually carried out either in basins of porcelain or platinum, or (when it is only a question of increasing the concentration) in glass vessels, especially boiling flasks, and unless there are reasons against it, the liquid is preferably heated to its boiling point. When boiling flasks are used the removal of the vapour may be accelerated by blowing a current of air through the vessel or by suction. A suitable current of air may be produced by using a retort with its neck inclined upwards and its tubulure open.

If in the use of basins for a long-continued evaporation there is a risk of the contents becoming contaminated by falling dust, etc., the basins should be covered over, but in such a manner that a space is left for the escape of vapour. A large glass funnel, which may be fixed in an inverted position over the basin by means of a clamp, is suitable for this purpose. It is fixed at an angle so that drops of liquid condensing on its side can drop from its lowest point into a vessel placed beneath it. Still better results are obtained by the use of Victor Meyer's protective funnel, which has its edges turned inwards, as shown in Fig. 11.

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[1] This is termed evaporation to dryness.

Instead of a funnel a glass plate or clock glass may be fixed in an inclined position over the basin by means of a clamp. Larger basins may be covered by washed[1] filter paper, which may be stretched across a double wooden hoop. This is clamped in a stand.

This precaution of covering the basin is only essential in the case of the most accurate work; it can usually be dispensed with if the evaporation is carried out in a dust-free place, preferably with the aid of suction, and in not too long a time.

Gas-burners are nearly always used for heating, a direct flame being applied beneath dishes, whilst wire gauze is placed between the flame and boiling flasks; if a more regulated heat is required as, for example, in the case of evaporation to dryness, recourse is had to water-baths, sand-baths, or iron or asbestos plates, which are heated with gas. Electrically heated plates, which can readily be maintained at constant temperature, are particularly suitable for this purpose. Further particulars are given in Sec. 19 (Heating apparatus). If it is a question of evaporation to remove inflammable organic solvents, such as alcohol, ether, petroleum spirit, or carbon bisulphide, care must be taken that the vapours are not ignited by the heating flame. In such cases electrically-heated plates or a water-bath with a small flame are used, or simply a vessel filled with hot water in which is immersed the flask containing the solution to be evaporated. It is advisable not merely to evaporate very volatile substances, but also to distil them from a slightly heated water-bath (Sec. 12), and to close the receiver with a stopper through which passes a tube communicating with the air outside.

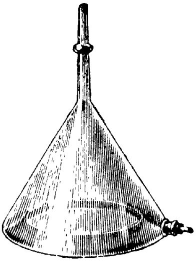

FIG. 11.

If the temperature should exceed 100° in the course of evaporation to dryness, spirting may easily occur through the formation of steam in the partially solidified residue. This may be prevented by stirring the mass with a glass rod.

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[1] To prevent the vapours, especially when they are acid, from dissolving from the paper compounds of iron, calcium, etc., which might then drop into the liquid.

To prevent the temperature exceeding 100° water-baths are used. Fig. 12 represents a simple form of water-bath, and Fig. 13 a form in which the water is always kept at a constant level by means of the connection with the water supply *a*, and an overflow pipe *b*.

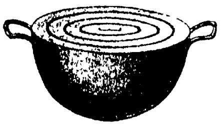

Fig. 12

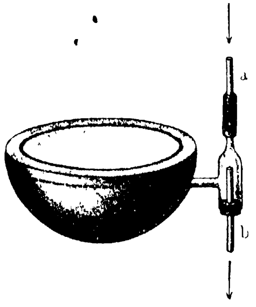

Fig. 13

Water-baths are provided with a series of copper or, better, porcelain rings fitting into each other, so that the opening can be made wider or narrower according to the circumference of the vessel to be heated.

A drawback in connection with evaporation is that porcelain dishes and glass vessels, the use of which can hardly be avoided in the evaporation of large quantities of liquids, are somewhat attacked, so that the liquid in question becomes more or less contaminated, and this interferes with more accurate analysis. We mention this point, which will be dealt with more fully in connection with quantitative analysis, only to call attention to the fact that alkaline liquids should not be evaporated in glass vessels, for at the boiling point they attack the glass to a considerable extent.

Hence specially resistant varieties of glass, such as the "Jena apparatus glass," which only have this drawback to a very slight extent, if at all, are now made for chemical work.

SEC. 12.

10. Distillation.

If a volatile liquid is converted into the form of vapour, but again condensed to a liquid which is collected, the process is termed distillation. By this means, as by the process of evaporation, it is possible to separate substances of different volatility from one another. Except in cases where the process is used to recover a volatile substance, distillation is used for the purpose of separating a very inflammable volatile liquid, *e.g.* ether, from a solution, so as to avoid the risk of igniting the vapours incurred in a simple evapora-

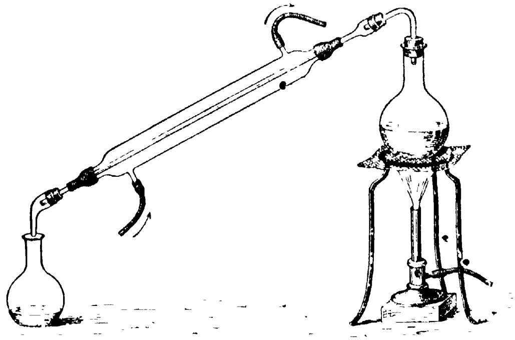

FIG. 14

tion. The apparatus required for carrying out a distillation consists firstly of a vessel in which the liquid is to be transformed into vapour (usually by heat), then of a connection in which the vapour is cooled and so condensed to liquid, and thirdly of a collecting vessel (receiver) for this liquid, known as the *distillate*.

Fig. 14 represents one of the commonest forms of laboratory distillation apparatus.

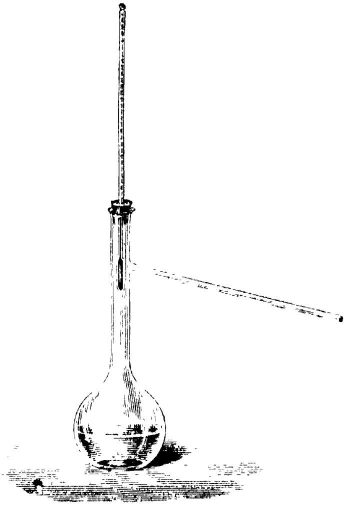

FIG. 15

Fig. 15 represents an apparatus, the distillation flask of which has a thermometer introduced into its neck. Since the vapours escaping from the boiling liquid sweep round the thermometer bulb, the boiling point of the liquid is shown. This temperature frequently affords a means of identifying a substance.

If several volatile substances are present in a liquid, it is, in many cases, impossible to separate the different individuals in accordance with their different volatility by means of distillation, since with the rise in the boiling temperature the vapours of the more volatile substances become mixed with those of the less volatile substances. The so-called *fractional* distillation (*i.e.* the separate collection of fractions distilling within definite limits of temperature, and their repeated redistillation), although it does not effect a completely quantitative separation, yet enables quite pure fractions to be obtained.

Inasmuch as fractional distillation is hardly ever used in qualitative analysis in the restricted sense in which it is dealt with in this book, but is mainly employed in the investigation of organic substances, with which we are not concerned here, a more detailed description of the process and an outline of the particular cases to which it is applicable are omitted.

Distillation is the process by means of which spring water or tap water, which invariably contains a more or less considerable quantity of dissolved substances (calcium, magnesium, sodium, carbonate, sulphate, chlorine ions, etc.), is freed from these for analytical purposes. For the preparation of *distilled water* in considerable quantities copper distillation vessels are used with cooling worms of pure tin. If the condensing tube is made of copper the water may easily be contaminated with that metal. It is best to keep distilled water in stoneware jars, and it must be protected from the influence of the laboratory air, from which it can readily absorb acid or ammoniacal vapours.[1] It is, therefore, advisable to make a routine practice of testing the purity of distilled water, in order to discover possible faults in the condensing worm. The durability of the latter is considerably increased by twisting strips of zinc round it, since these form a galvanic protection against the action of the cooling water. Smaller quantities of distilled water are prepared in glass flasks, but it is advisable to use a condenser of resistant (*e.g.* Jena) glass.

SEC. 13.

11. Ignition.

If it is required to remove from solid substances their volatile constituents, the same means as described in the case of evaporation may be used to convert them into the form of vapour. As a rule a degree of heat varying with the volatility of the substance to be removed is applied, and the process may be described as gentle heating, heating (*e.g.* in drying), or ignition.

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[1] The distilled water in washing-bottles invariably contains carbon dioxide derived from the bubbles of air breathed into it, and it is necessary to remember this in certain cases.

Thus carbon dioxide may be expelled from calcium carbonate (kilning of lime) and water from calcium hydroxide by ignition, and ammonium salts may be removed in the same way from a mixture of salts which contains them.

In addition to being ignited for this purpose, substances are also sometimes ignited to change their condition without causing them to volatilise, as, for example, in the conversion of a loose clay readily soluble in sulphuric acid into a hard baked mass less soluble in sulphuric acid. Lastly, in analytical work the substance under examination is often ignited, so as to obtain data from its behaviour at the ignition temperature for conclusions as to its general nature, its resistance to heat, its fusibility, or the presence or absence of organic substances, etc.

Crucibles are the vessels ordinarily used for ignition. For analytical purposes smaller crucibles or small flat dishes (crucible lids) of porcelain, platinum, silver, iron, quartz glass, or glass tubes fused together at one end are used according to the conditions. These are heated over a strong gas flame or sometimes over a blowpipe flame, or in many cases in an electric oven.

For details as to the methods of using crucibles, see the end of Sec. 15, pp. 58 and 59, and with reference to the heating, see Sec. 19.

SEC. 14.

12. Sublimation.

When solid substances are converted, by heating, into vapours which are then condensed again by cooling, the process is termed sublimation, and the volatilised and recondensed substance a *sublimate*. Whether a substance melts when heated and then, as the temperature rises, boils (or distils), or whether it sublimes without melting, depends upon whether its vapour pressure even at a temperature below its melting point is equal to the atmospheric pressure (when it sublimes) or whether it is not equal to it until after the melting point has been passed (when it melts and distils). In practice, however, it is usual also to speak of sublimation when the condensed substance solidifies again at the ordinary temperature. Thus, for example, sulphur when heated first melts and then distils, and solidifies again on cooling to the ordinary temperature. If the experiment is tried on a small scale a sublimate is obtained in which the minute drops first formed may still be plainly observed.

As a rule sublimation is used for the separation of different volatile substances. In analysis it is of the greatest importance for the identification of many substances, *e.g.* arsenic. The form of sublimation vessels varies widely according to the volatility of the substance. Sublimation for analytical purposes is, as a rule, effected in a small glass tube closed by fusion only at one end. When the sublimation is to be carried out in a current of hydrogen or carbon dioxide, a tube open at both ends, and usually constricted beyond the place to be heated, is used, into which the substance to be sublimed is introduced either directly or in a platinum or porcelain boat.

SEC. 15.

13. Melting, Decomposition, and Explosive Fusion.

By *melting* is understood the conversion of a substance into the fluid condition under the influence of heat. It is a property of every substance at a definite temperature, and its determination may be used for the recognition or identification of the substance.

The test is frequently employed, especially in the case of organic substances. The usual method is to place a small quantity of the substance in a narrow glass tube drawn out to a still finer tube, the bottom of which is closed by fusion. This is attached by means of a narrow rubber band to a thermometer in such a way that the part containing the substance under examination is at the same level as the mercury bulb. Both are immersed in a suitable bath and heated together, and the reading of the thermometer is taken at the moment when the substance is seen to melt in the narrow tube. For other methods of determining the melting point reference may be made to the *Zeitschrift für analytische Chemie.* The presence of foreign bodies usually lowers the melting point of a substance (*cf.* p. 30).

If a solid substance is introduced into a melted one, or if a mixture of two or more substances is heated until one of them melts, reactions may take place between the now fluid substance and that which has not yet melted at the temperature reached, as described in Sec. 3; *i.e.* in so far as there is any action at all, there may either be simple solution or a chemical reaction accompanied by solution. Instances of the first process are to be found in the melting together of fats or resins, and also of metals (in which case chemical compounds are, of course, frequently formed); whilst examples of the latter process are afforded by the fusion of barium sulphate with sodium carbonate. This is the form in which the process is mainly used for analytical purposes.

When substances which are insoluble or dissolve with difficulty in water and acids are altered or decomposed by fusion with other substances in such a way that they, or rather the new compounds produced, are rendered soluble in water or acids, the process is termed *decomposition.*

Substances for the analysis of which the process of decomposition is particularly necessary, include the sulphates of the alkaline earth metals, many silicates, and many aluminium compounds. The ordinary fusion agent is sodium carbonate or potassium carbonate, or better still, a mixture of the two in the proportion of their molecular weights, which melts more readily than the separate alkali carbonates In certain cases barium hydroxide may be used in place of alkali carbonate. Potassium hydrogen sulphate, or sodium hydrogen sulphate, is also frequently employed for the decomposition of ignited oxides, etc. In the case of these two latter fusion agents the temperature must not be raised too high, for their action depends upon the fact that they decompose into neutral alkali ulphate and free sulphuric acid. The latter thus acts more effectively at this higher temperature than if the substance were boiled with concentrated sulphuric acid. But if the temperature is raised beyond the point at which even slight white fumes of sulphuric acid re visible, the sulphuric acid escapes, and the fused mass loses its most active constituent. Hence the heating is continued for a long time, but only at a temperature sufficient to keep the mixture fused, nd the crucible is kept covered [1]

Metals and the residues left on dissolving metals in nitric acid re frequently fused with a mixture of sodium carbonate and sulphur, r with the "liver of sulphur," prepared by the previous fusion of hese two substances. The process is preferably carried out in a orcelain crucible, which to prevent loss of sulphur is kept covered.

When it is desired in the process of fusion or decomposition to ffect simultaneous reduction or oxidation (*cf.* Sec. 16), substances re used as the fusion agents or are mixed with the fused mass, hich are capable of absorbing oxygen (potassium cyanide, sodium formate, etc.) or of liberating it. Of the latter special mention may be made of alkali nitrates, chlorates, ferroxides, persulphates, and percarbonates. When they are used the reaction may be intensified almost to an explosive degree. This is known as "explosive fusion."

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[1] If the mass has been heated too strongly before decomposition is complete, may be allowed to cool, strong sulphuric acid added so that hydrosulphate is gain formed, and the heating repeated.

The aim of this form of fusion is either to obtain the oxidation product (as, for example, when arsenic sulphide is fused with potassium nitrate to obtain potassium arsenate), or it is used as a means of proving the presence or absence of a substance (as when, for example, a test for nitrates or chlorates is applied, by observing whether the substance under examination behaves explosively when fused with potassium cyanide, etc.). In the first case the absolutely dry mixture of the substance and the explosive agent is introduced little by little into a red-hot crucible. For the latter kind of tests only small quantities should be used, preferably on thin iron or platinum foil or in a small metal spoon.

In analytical processes fusion and decomposition is carried out, according to the conditions, in crucibles of platinum, silver, or nickel, which are fixed in a triangle resting on the ring of a suitable stand over a gas, spirit, or petrol lamp (see Sec. 19). Fusions on a smaller scale are also frequently carried out in a small glass tube closed by fusion at one end. With regard to bead reactions, see Sec. 21.

The choice of the crucible to be used depends upon the nature of the substance to be fused.

Platinum crucibles are for most purposes the most resistant. In the cases mentioned below, in which they cannot be used, porcelain crucibles are usually employed, but have the disadvantage that allowance has to be made for their glazed surface being attacked to a certain extent by the fusion agents. Alkali hydroxides and peroxides have a very pronounced action upon porcelain crucibles, and crucibles of nickel or iron (or silver in the case of alkali hydroxides) must be used with these fusion agents. Silver crucibles will not stand being heated to a high temperature.

Different forms of triangles are used according to the nature of the crucible material. Porcelain, nickel, iron, and silver[1] crucibles may be fixed in a triangle of iron wire; platinum crucibles will be attacked by the iron. In such cases platinum wire triangles (Fig. 16) are used, or iron triangles with platinum points projecting inwards on each of the sides;[2] or triangles, the side wires of which re passed through small tubes of biscuit porcelain (clay pipe stems) r of quartz glass. If these small tubes are too thick they prevent he free access of the flame to the crucible; this drawback is bviated in the form of pipeclay triangle hown in Fig. 17.

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[1] Silver crucibles must not be placed in platinum triangles, or an alloy will be formed.

[2] *Zeitsch. anal. Chem.*, **39**, 651.

Decompositions with alkali carbonates, or with barium hydroxide, or alkali hydrosulphates are carried out in platinum crucibles.[1]

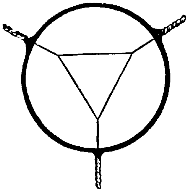

FIG. 16.

A brief outline may be given here of ertain precautionary rules to be followed to rotect platinum vessels from injury. No ubstances which emit chlorine[2] must be eated in platinum vessels. Alkali nitrates,[3] ydroxides or cyanides, metals and sulphides must not be fused n them, nor must they be used for the ignition of readily reducible metallic oxides, salts of heavy metals with organic acids, nd phosphates in the presence of organic compounds. Lastly, latinum crucibles are injured by being heated in a luminous and herefore smoky flame. This renders the platinum soft and brittle hrough the formation of platinum carbide. Moreover, care must be aken that a platinum crucible which has been brought to white eat over a blow-pipe flame is ot suddenly exposed to a blast f cold air by rapidly cutting off he gas supply, or it may easily ecome slightly cracked. Dirty latinum crucibles may be cleaned with moist sea sand, the granules f which are rounded and do ot scratch. If spots are left which cannot be removed in this way, potassium hydrosulphate or orax is fused in the crucibles, the mass boiled with water, and the rucibles again polished with sand.

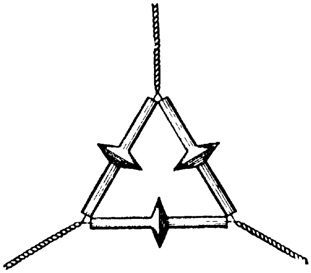

FIG. 17.

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[1] Platinum is somewhat attacked in fusions with alkali carbonates, so that mall quantities of the latter may be found in the fused mass (L. L. de Koninck, *Zeitsch. anal. Chem.*, **18**, 569).

[2] Hence, *e.g.* fused masses which contain nitrates must not be dissolved out of the crucible with hydrochloric acid, but must be soaked in water and separated from the crucible before being treated with acid.

[3] When they are not mixed with a corresponding quantity of alkali carbonate.

Cold fused masses may be detached from platinum crucibles either by making the crucible red-hot and placing it on a thick cold iron plate (when cold, the mass usually separates cleanly from the platinum, although the crucible may readily be injured in this way), or after complete cooling the crucible is again heated until the edge of the fused mass again begins to melt, once more cooled, and, after the addition of sufficient water to cover the mass completely, again heated over a flame. If the crucible is free from rough points the fused mass will now dissolve cleanly from the interior of the crucible.[1] It is not advisable to loosen the fused mass by pressing the sides of the crucible.

SEC. 16.

14. Oxidation and Reduction.

By oxidation in the more restricted sense is understood the combination of a substance with oxygen; by reduction the reverse process, the separation of a substance previously combined with oxygen from this combination.

The combustion of carbon (charcoal) to form carbon dioxide, of hydrogen to form water, and the formation of lead oxide by heating metallic lead in the air are oxidation processes, whilst the separation of mercury on heating mercury oxide is a reduction process.

In many cases both these processes take place simultaneously. When iron ore (ferric oxide) is heated with carbon (charcoal) the iron oxide is reduced to metallic iron, whilst the carbon is oxidised to carbon monoxide or dioxide. In this case the carbon is termed the reducing agent (which is itself oxidised) and the iron oxide is the oxidising agent (which itself undergoes reduction).

In a *wider* sense the terms are also applied to analogous processes, the combination of a metal with chlorine or with acid radicles in general, for example, being described as oxidation, and the separation of a metal from such a combination as reduction.

According to this the precipitation of a copper from a cupric sulphate solution by metallic zinc is to be regarded as analogous to the ignition of iron oxide with carbon. The zinc acts as a reducing agent, and is oxidised to zinc sulphate, the copper sulphate as an oxidising agent, and is reduced to copper.

Since, as was explained above (p. 24), it is a matter of indifference which anion is present in such processes, one can also say here that metallic zinc is the reducing agent (being oxidised to zinc ion), and that the cupric ion is the oxidising agent (being reduced to metallic copper).

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[1] Stockmann, *Zeitsch. anal. Chem.*, **15**, 283.

In all the examples cited above the oxidation may be represented as a manifestation of the previously unexercised valencies of a metal or in general of an electropositive substance, through its combination with an electronegative one (oxygen, acid radicle), or through its conversion into the cation condition; whilst the reduction may be represented as the separation of the electropositive substance from the combined (cation) condition in an elementary form.

If an electropositive substance forms a series of compounds in which it is present with different valency, the conversion of the lower states of valency into the higher is an oxidation process, and the conversion of the higher into the lower state a reduction process.

When ferrous oxide is converted by ignition with oxygen into ferric oxide, there is undoubtedly an oxidation process in the strictest sense:

$$2FeO+O=Fe_2O_3.$$

Hence by analogy the reaction of the conversion of ferrous chloride into ferric chloride, $2FeCl_2+Cl_2=2FeCl_3$, is also an oxidation process.

Expressed as an ion formula this process may be represented as $2Fe''+Cl_2=2Fe^{\cdot\cdot\cdot}+2Cl'$, *i.e.* the ferrous ion is oxidised to ferric ion, while a new cation charge is given to it. The oxidising agent chlorine is reduced, while it changes its condition from that of an element into that of an anion.

If, on the other hand, stannous chloride is made to act upon ferric chloride, the latter is reduced to ferrous chloride, whilst the former is oxidised to stannic chloride:

$$2FeCl_3+SnCl_2=2FeCl_2+SnCl_4, \text{ or } 2Fe^{\cdot\cdot\cdot}+Sn^{\cdot\cdot}=2Fe^{\cdot\cdot}+Sn^{\cdot\cdot\cdot}.$$

The oxidation here consists in the formation of cation, *i.e.* the increase in the cation charge of the tin, whilst the reduction consists in the discharging of the ferric cation to leave ferrous cation.

If, in the oxidation of ferrous chloride to ferric chloride, elementary chlorine has an oxidising action, in which it is reduced to chlorine anion, its action upon, *e.g.* potassium iodide, in which it is also reduced to the anion condition while liberating free iodine, must also be an oxidising action:

$$2KI+Cl_2=2KCl+I_2, \text{ or } 2I'+Cl_2=I_2+2Cl'.$$

In this case, then, the oxidation is a discharge of an anion, and the reduction the formation of an anion.

Speaking generally, therefore, the following statements may be made: An electropositive substance (*e.g.* hydrogen or a metal) is oxidised (acting for its part as a reducing agent) when it exerts its valency (when, in aqueous solution, it forms anions). It is reduced when it is separated from a compound (when, in aqueous solution, its cations are discharged).

An electronegative substance (oxygen, chlorine, acid radicle) has an oxidising action (is itself reduced) when it exerts its valencies (when, in aqueous solution, it forms anions). It is oxidised (has a reducing action) when it is liberated from its compounds—when its anions are discharged.

As was pointed out on p. 31, the metals may be arranged in an order of tension in the sense that those which come first in the series invariably precipitate from their compounds those which follow. This is a consequence of the differences in the degree of electro-affinity; the less "noble," more positive metal always acts as a reducing agent upon the compounds of the more "noble," less positive metals. Thus, for example, copper precipitates silver from silver solutions, but is itself precipitated from its solution by zinc.

There is also a similar series in the case of electro-negative substances in which the more strongly negative always has an oxidising influence on the more weakly negative, and forces it out of its combinations.

Thus chlorine liberates bromine from bromides (*i.e.* oxidises them), whilst bromine has an oxidising action upon iodides, *i.e.* liberates iodine from them.

Oxidation processes, however, may also follow such a course that a negative substance such as oxygen exerts its valencies upon a substance which otherwise has a negative action, *e.g.* sulphur, which is oxidised with the formation of sulphur dioxide, or, when more strongly oxidised, yields sulphur trioxide:

$$S+O_2=SO_2 ; \quad 2SO_2+O_2=2SO_3.$$

In this case sulphur has an electropositive action towards oxygen.

Characteristic instances of this are the reduction of nitric acid to ammonia by hydrogen (zinc or iron with hydrochloric acid):

$$HNO_3+8H=NH_3+3H_2O.$$

In this case the nitrogen in combination with negative oxygen towards which it has a positive action) is liberated from that combination, and then combines with the positive hydrogen (towards which it behaves as a substance with a negative action), and, in the widest sense of the term, oxidises it.

The fact that oxidation and reduction processes are very frequently associated with the formation or discharge of ions affords an explanation of the well-known observation that a substance has a stronger action at the moment of liberation (*in statu nascendi*). The separate ions which have been liberated from the molecular combination, and have not yet reunited to form another molecule, can then be exceptionally active. Thus, in the example last mentioned the reduction is effected by the hydrogen *in statu nascendi*, whereas elementary hydrogen does not have this effect. The energetic oxidising action of ozone (*i.e.* of the modification of oxygen containing three atoms in its molecule) is also obviously to be attributed to the fact that an atom is readily split off from the ozone molecule, and that the free atoms are able to exert their electropositive characteristics to a much more pronounced extent than when they are in combination in the molecule.

Oxidation and reduction processes may play various parts in chemical reactions.

Two dissolved substances may react with each other, and both products of the reaction remain in solution, as *e.g.* in the case of the action of stannous chloride upon ferric chloride: $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$. Or one of the substances may be precipitated, as *e.g.* in the action of stannous chloride upon mercuric chloride, in which mercurous chloride is precipitated: $2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$.

Again, a solid substance may be dissolved, and the products of the reaction may then either remain in solution, as *e.g.* in the reduction of ferric chloride by zinc: $Zn + 2FeCl_3 = FeCl_2 + ZnCl_2$; or may be partially separated as a solid substance (as in the precipitation of copper by zinc): $Zn + CuSO_4 = ZnSO_4 + Cu$; or may partially escape in the form of gas (*e.g.* as in the solution of zinc in acid): $Zn + H_2SO_4 = ZnSO_4 + H_2$.

Or a gas may act upon a solution, as *e.g.* sulphur dioxide upon an acid chromate solution: $3SO_2 + H_2Cr_2O_7 = Cr_2(SO_4)_3 + H_2O$ (in this case everything remains in solution); or as in the case of the action of hydrogen sulphide upon ferric chloride: $2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$ (in which case sulphur is expelled by the chlorine ion and is precipitated).

Two substances may also act upon one another in the fused condition (see p. 56).

Solid substances may interact, as in the metallurgical separation of metals by ignition with charcoal, whilst gases may act upon solids, upon liquids, and upon other gases, as in combustion, reduction in a current of hydrogen, etc.

A description of the different methods used in carrying out oxidation and reduction processes may be omitted here, since they are dealt with in connection with all the other processes (*cf.* in particular, Sec. 15, p. 57; Secs. 20 and 21, flame reactions, bead tests, blowpipe tests).

It only remains to be mentioned that in accordance with the definition given above, whereby oxidation consists in the formation of cations, or the discharge of anions, an oxidation process invariably takes place in electrolysis at the positive pole, the anode, whilst there is a reduction process at the cathode, where cations are discharged or anions formed. In this case the two parts of the complementary process are spacially separated. Occasionally the oxidising or reducing action of electrolysis is used even in qualitative analysis.

SEC. 17.

15. Neutralisation, Determination of the Reaction of a Solution.

Solutions of acids contain hydrogen ions. They have a sour taste, and dissolve metals, etc. Solutions of bases contain hydroxyl ions; they are termed alkaline (because only the hydroxides of the alkali and alkaline earth metals are soluble in water to any material extent), they have a characteristic so-called soap-lye[1] taste, and when sufficiently concentrated have a corrosive action.

If equivalent quantities of acids and bases (*i.e.* such as contain or can liberate corresponding quantities of hydrogen and hydroxyl ions) are made to react with each other, these hydrogen and hydroxyl ions combine to form water,[2] and the acid radicles and metals present unite to form salts, or remain as anions or cations in solution.

Such a salt or salt solution is neither acid nor alkaline; it is therefore termed neutral and the process of the reciprocal saturation of acid and base neutralisation.[3]

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[1] The name originated from the fact that solutions of alkali hydroxides are termed "lyes," as, for example, potash lye (KOH solution), soda lye (NaOH solution).

[2] The solution then contains only as many hydrogen and hydroxyl ions as does pure water. These need not be taken into account in the following outline.

[3] Neutralisation between acids and bases may also obviously occur when one of the two constituents is a solid, as *e.g.* in the interaction of solid calcium hydroxide and hydrochloric acid, or of solid tartaric acid and sodium hydroxide

The reaction takes place in this way when acids and bases of equal strength are brought into contact.

But if a strong acid is made to act upon a weak base, or, on the other hand, a strong base upon a weak acid, hydrolysis, as described on pp. 27, 28, takes place; *i.e.* notwithstanding the fact that the quantities of metal and acid radicle correspond, and may also yield in solid form (*e.g.* by evaporating the solution) a neutral salt, as defined in Sec. 19; yet if the solution contains more hydrogen or hydroxyl ions than does water, it will show an acid or alkaline character. It is, therefore, necessary to add a more or less considerable excess of the weak constituent to establish a condition of equilibrium, in which the solution contains no hydrogen or hydroxyl ions, *i.e.* is of neutral character as defined above

In analytical practice the acid, alkaline, or neutral condition of a solution is recognised by its behaviour towards certain colouring matters of natural occurrence obtained from plants, such as litmus or turmeric, or artificially prepared ones, such as methyl orange or phenolphthalein. These colouring matters are termed indicators, and the colorations which acid, alkaline, or neutral solutions give with them are termed the *reaction* of the solution Hence a particular solution is said to have an acid, alkaline, or neutral reaction.

In qualitative analysis indicators are used almost exclusively in the form of strips of paper, test papers, which are saturated with the particular colouring matter. This is moistened with the liquid under examination [1] (the test paper is dipped into it), and any change of colour noted.

Litmus colouring matter is naturally blue, but is turned red by acids. Turmeric is yellow, and is changed to brown by alkaline liquids. Methyl orange is yellow, and becomes red with acids. Phenolphthalein is colourless, and is changed to red by alkaline liquids, although it is again decolorised by *very* strong alkaline solutions.

As a rule the only test papers used are blue and red litmus paper (the latter being turned blue by alkaline solutions) and yellow turmeric paper.

The change of colour in indicators depends upon the fact that the colouring matters in question are acids, the ions of which are of a

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solution. An acid may also be neutralised by the action of a carbonate, because the free carbonic acid liberated by the other acid is decomposed into water and carbon dioxide, which latter escapes.

[1] In testing alcoholic liquids the litmus paper must first be moistened with water.

different colour from that of the undissociated acid molecules. In acid solutions their dissociation is prevented by the hydrogen ion concentration of the solution, and the colour is that of the undissociated molecule. In alkaline liquids the molecules of the colouring matter are dissociated, and the colour of the ions is manifested.[1]

The prevention of the dissociation (*i.e.* the change of the ion coloration into that of the undissociated molecules) corresponds to a proportion of hydrogen ions in the liquid under examination, varying according to whether the indicator is a stronger or weaker acid.

Thus methyl orange is a relatively strong acid. It is not sensitive towards weak acids (*i e.* does not give a red coloration with them). On the other hand, phenolphthalein is a weak acid, the dissociation of which is readily prevented. Hence the red colour of its ions disappears as soon as the solution contains more hydrogen ions than correspond to pure water. It is, therefore, sensitive towards weak acids

The difference between the two indicators becomes obvious, *e g.* in the neutralisation of phosphoric acid. When sodium hydroxide is added to an aqueous solution of phosphoric acid a change of colour is indicated by methyl orange, if sodium dihydrogen phosphate, NaH_2PO_4, is formed, whereas such a solution still shows an acid reaction towards phenolphthalein; but if more sodium hydroxide is added the colour changes to red, as soon as the whole of the phosphate has been converted into disodium hydrogen phosphate, Na_2HPO_4.

Conversely, methyl orange is sensitive towards weak bases, whilst phenolphthalein is insensitive.

Litmus colouring matter occupies an intermediate position between methyl orange and phenolphthalein as regards its acid character, whilst turmeric colouring has about the same character as phenolphthalein.

A detailed description of these characteristics would be of relatively little importance in connection with qualitative analysis. This point will be dealt with more fully in connection with the volumetric processes of quantitative analysis, in which indicators play a very important part.

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[1] The dissociation into ions is accompanied by an inner transformation in the colouring matter molecule, upon which the actual change of colour depends.

SEC. 18.

16. The Generation and Use of Gases.

The generation of a gas, *i.e.* the evolution of a gaseous substance, invariably takes place when a chemical reaction occurs in which a gas is produced, as, for example, in the decomposition of potassium chlorate by heat into potassium chloride and oxygen: $KClO_3 = KCl + 3O$; or in the solution of calcium carbonate in hydrochloric acid, in which carbon dioxide is evolved: $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$; or when in the solution of a gas the conditions (pressure or temperature) are so altered that the gas can no longer remain in solution, as *e.g.* in the reduction of pressure on opening a bottle of soda-water.

This last case hardly ever occurs in analytical chemistry, except in connection with the separation of dissolved gases (carbon dioxide, hydrogen sulphide, etc.) from a liquid. This is nearly aways done by boiling the gas out of the liquid The evolution of gases in chemical reactions may afford the means of detecting the presence of substances which under definite conditions escape in gaseous form, and it is also of importance when a gas is to be used as a reagent and is prepared for that purpose.

Obviously the process is essentially the same in each case, the only difference being that in the latter case it is carried out upon a somewhat larger scale.

The methods most frequently employed in the preparation of gases for analytical purposes are all based upon the action of an acid upon a solid substance. For example, carbon dioxide is generated from marble and hydrochloric acid, hydrogen from zinc and sulphuric acid, hydrogen sulphide from iron sulphide and hydrochloric acid. We, therefore, restrict ourselves here to a description of these methods. Details of other methods of generating gases (*e.g.* the generation of hydrogen by heating sodium formate) will be given in the appropriate places.

For the generation of gas from a solid substance and a liquid (almost invariably an acid), the apparatus almost exclusively used at the present time are those with continuous action, *i.e.* those in which the current of gas is interrupted by using the pressure of the gas itself to separate the liquid from the solid substance, but in which, by simply turning a tap, gas may be withdrawn and the evolution of gas started again.

An extraordinary number of methods of utilising this principle have been devised, but only the very extensively used apparatus of Kipp, illustrated in Fig. 45 (Sec. 89), will be described here, and for details of other forms of apparatus reference may be made to the *Zeitschrift fur analytische Chemie.*

Kipp's apparatus consists of three globular vessels arranged one above the other. The lowest of these has a base upon which the whole apparatus stands, is provided with a side tubulure closed by a stopper, and is connected by means of a fairly long neck with the middle bulb. The latter also has a tubulure in the upper part of its side, and the outlet tube for the gas is passed through the perforation in a stopper fixed in this opening. The long lower tube of the topmost bulb is inserted into a ground-in joint in the neck of the middle bulb. This long tube passes right through the middle bulb and extends to a considerable depth into the lowest bulb. The space between the tube and the neck, which separates the two lower bulbs, must be so narrow that no portions of the solid substance used in generating the gas can fall to the lowest part of the apparatus. If necessary, this may be prevented by surrounding the tube with a strainer of acid-proof material. The middle bulb is charged with the solid generating substance through the side tubulure. The acid is then poured into the top bulb so that it fills the lowest and rises into the middle bulb. When it comes into contact with the solid substance the evolution of gas begins. Air is first expelled from the apparatus by means of the gas, and the latter may then be allowed to flow through the outlet tube in a current regulated by the tap. When the tap is closed the pressure of the gas drives the acid downwards and then through the central tube into the upper bulb. The heavy salt solution formed in the generation of the gas sinks to the bottom of the lowest bulb, so that until it reaches the bottom of the tube fresh acid is continually brought into contact with the solid substance. The salt solution is drawn off through the tubulure of the lowest bulb.

Should it be necessary before using a gas to free it from entangled particles of liquid from the generator, or from moisture, or other gases present as impurities, it is made to pass through washing flasks containing suitable liquids. This has the further advantage (and this also applies to cases where the gas is not passed through absorbent liquids) that the strength of the current of gas can be estimated from the number of gas bubbles. A simple form of washing flask is represented by *c* in Fig. 45. A double washing flask is shown in Fig. 18, in which an overflow of liquid from one direction, or a rushing back of the washing liquid from the other direction is impossible. As a rule, concentrated sulphuric acid is used for drying a gas.

The presence of foreign gases, which under certain conditions may interfere with the use of a gas, is due to the use of impure materials. Thus, for example, hydrogen sulphide (removable by washing the gas with potassium permanganate solution) occurs in carbon dioxide when marble containing pyrites is used.

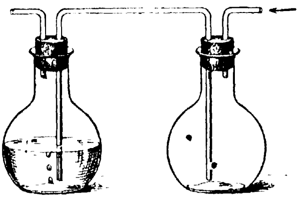

FIG. 18.

Carbon dioxide is generated from marble and hydrochloric acid of sp. gr. 1·05. *Hydrogen* is generated from zinc and sulphuric acid of sp. gr. 1·18. The use of too concentrated acid makes the liquid too hot, and may result in the formation of sulphur dioxide, or under certain conditions, of hydrogen sulphide. Hydrogen is purified by washing it with solutions of sodium hydroxide permanganate and silver nitrate, through which the gas is made successively to pass. It is only under quite exceptional circumstances that hydrogen is absolutely free from traces of arsenic. (For further particulars, see Sec. 89, 12, where also will be found directions for overcoming the difficulty that absolutely pure zinc is very resistant to the action of dilute sulphuric acid.)

When substances are to be heated in a current of hydrogen care must be taken that all the air has first been expelled from the generating apparatus and tubes. The gas is, therefore, allowed to escape for some time, and a test may then be made by collecting

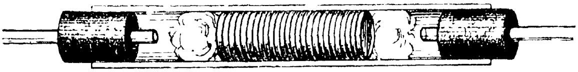

FIG. 19.

some of it in a test tube and applying a light to ensure that it no longer consists of an explosive mixture. The safety tube devised by R. Fresenius, and represented in Fig. 19, may also be used as a safeguard against a possible explosion of a gaseous mixture within the apparatus. This tube contains discs of wire gauze compressed between wads of cotton wool. Its action is based on the principle of the *Davy* safety lamp. In order that it may be trustworthy it is essential that the wire gauze discs shall be exactly the same size as the inner diameter of the tube, so that no passage shall be left free for the explosion, and also that the layer of discs shall be of sufficient length (about 5 cm.). A strong caution must be given against the use of badly constructed safety tubès not complying with these conditions.

The generation of *hydrogen sulphide* is particularly important in analytical work.

As a rule it is prepared from iron sulphide and hydrochloric acid (of sp. gr. 1·05). Since the iron sulphide and hydrochloric acid (which may be crude acid, *i.e.* not chemically pure) are never entirely free from arsenic, traces of hydrogen arsenide may be present in the hydrogen sulphide, and cause traces of arsenic sulphide to appear in the precipitates produced by the hydrogen sulphide. It is only in particularly delicate investigations, however, in which attention must be paid to the slightest trace of arsenic, that it is necessary to take this source of error into consideration.

For such work the iron sulphide may be replaced by barium sulphide, prepared by igniting heavy spar with carbon, or by calcium sulphide, which may be obtained from gypsum and carbon. (See also, *e.g.* R. Fresenius, *Zeitsch. anal. Chem.*, **26**, 339 ; and Sec. 202, 3)

Hydrochloric acid containing a considerable amount of arsenic must not be used, since otherwise so much hydrogen arsenide will be present in the hydrogen sulphide that arsenic sulphide will be deposited in the tubes conducting the gas. Any considerable proportion of selenium in the hydrochloric acid may also produce abnormal results. The presence of selenium is indicated by the appearance of an orange-red precipitate in the generating flask.

In larger analytical laboratories so much hydrogen sulphide is required that the ordinary Kipp's apparatus is not large enough for the purpose. Fig. 20 represents a form of apparatus devised by Brugnatelli, which, with certain modifications, has been used for many years with good results in the author's laboratory.

The flask *B*, which is provided with a tubulure *a*,[1] has its neck filled with coarse fragments of glass, whilst small lumps of iron sulphide are introduced into its body. Through the rubber stopper are passed the tube *s* (which under certain conditions may be omitted, *vide infra*) and a short tube *c*, of at least 1 cm. in diameter, which is connected by means of a short piece of rubber tubing with the tube *d* passing through the stopper of the flask *A*. The tube *c* extends nearly to the bottom of *A*, and is connected at its other end with the flask *M* by means of the tube *f*, through the stopper of which passes a short glass tube open at each end. The stopper of the tubulure *a* of the flask *B* also has a tube attached by rubber tubing to the lead

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[1] Flasks with a side tubulure, such as are frequently used as receivers, are also applicable for this purpose, as shown in Brugnatelli's original sketch (*Zeitsch. anal. Chem.*, **6**, 389), but are less suitable.

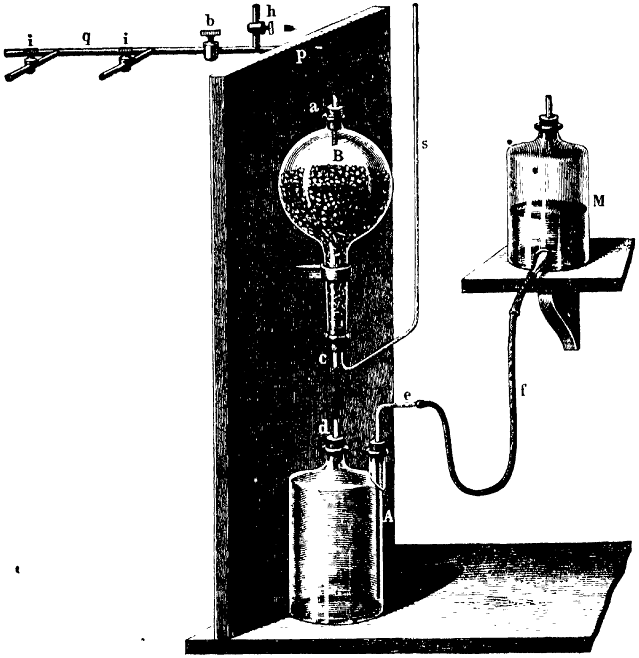

FIG. 20.

tube *q*, which is provided with brass taps, *h*, *b*, *i*, *i*, through which the gas may be conveyed to different places.

In using the apparatus the tap *h* is opened and a mixture of one volume of crude hydrochloric acid (as free from arsenic as possible) and two volumes of water is introduced into *M*. The liquid reaches *A*, and rises through *d* and *c* into the flask *B*. As soon as it has nearly filled the neck the tap *h* is closed, care being taken that *M* is then only about half full. On now opening the tap *b* and one of the taps *i*, the acid rises up to the iron sulphide in *B*, the evolution of hydrogen sulphide begins, and continues in a uniform manner, owing to the fact that the wide tubes *c* and *d* allow the heavy ferrous chloride solution to fall continuously, while fresh acid rises to the iron sulphide. To increase the amount of contact between the acid and iron sulphide one or more blocks are placed below *M*, whereby the pressure of the liquid is augmented. The current of gas may thus be regulated at will by raising or lowering the flask *M*, as Brugnatelli recommends, but when the apparatus is required for supplying the gas simultaneously to different liquids, as is the case in large laboratories, the use of taps is necessary.

If the apparatus is not to be used for some considerable time the flask *M* is placed at a lower level. The liquid then falls in *B*, and is no longer in contact with the iron sulphide, so that the evolution of gas gradually ceases. If at this stage hydrogen sulphide is not developed rapidly enough to fill the space left by the liquid, air is drawn through the tube *s*. This tube (if used at all, *vide infra*) is preferably fairly long, to prevent liquid being forced out from it, when the hydrogen sulphide has to overcome the pressure of a higher column of liquid. Should any hydrogen sulphide still be developed from the moist iron sulphide after removal of the acid, the only result is that somewhat more acid flows from *A* to *M*.

The tube *s* may be omitted when taps are used. In that case the liquid in *B* falls more slowly when *M* is placed in a lower position, because the space of the receding acid is then occupied by hydrogen sulphide; but in the absence of a tap the tube *s* is necessary to prevent the liquid into which the hydrogen sulphide is being introduced from being sucked back when *M* is placed in a lower position. Obviously this drawback is readily obviated when taps are used by closing *b* before lowering *M*. The gas delivered from *i* and *i* is conducted through washing flasks, or in winter through U-tubes packed with cotton wool.

When the acid is finally spent, *M* is placed at a lower level than *A*, and the tap *h* (when the tube *s* is omitted) is opened. The whole of the liquid then flows into *M* and can be poured away.

If a *Woulfe* flask with three necks is used as the vessel *A*, a siphon tube with a pinchcock may be fixed in the third of these, and the ferrous chloride solution collecting at the bottom of the vessel be drawn off at intervals. In this case, the lower limb of the tube *e* is made of such length that it only reaches halfway down into *A*, so that the acid flowing back into the flask does not mix with ferrous chloride solution.

Other forms of large apparatus have been described by C. Winkler[1] and Kuster.[2]

A large glass carboy of 50 to 60 litres (acid carboy) has been suggested by H. Lohndahl[3] and Wohlk[4] as the vessel for equalising the pressure in the case of apparatus delivering gas at several points.

Hydrogen sulphide apparatus, especially such as used for the production of large quantities of gas, must be placed either in the open or in well-ventilated rooms. The taps through which the supply of gas is drawn should be fixed within a fume cupboard, for hydrogen sulphide is not only an unpleasant gas, but *if inhaled in the undiluted form* may also immediately produce pronounced effects of poisoning. When carefully used, however, it is quite innocuous. The hydrogen sulphide is conducted through glass tubes into the liquid under examination, and care must be taken that the column of liquid is not higher than corresponds to the pressure within the generator.

As a rule, a moderate current of gas is sufficient; for, obviously, the unabsorbed portions have no action. Only in exceptional cases, which will be dealt with in their place, is a stronger current of gas necessary. To avoid the use of an excessive quantity of hydrogen sulphide Grabe recommends that the tube introducing the gas into the liquid under examination should be passed through a stopper (cork), which will fit the neck of the vessel containing the liquid. Gas is introduced, while the cork is placed loosely in the neck, until the air above the liquid has been expelled; the cork is then fitted tightly into the neck, leaving the other end of the tube in free communication with the gas generator. In proportion as the liquid absorbs the hydrogen sulphide above its surface more gas can enter into the flask. This suggestion, so far as we are aware, has not yet been widely adopted.

In cases where only a small amount of hydrogen sulphide is required, a saturated solution of the gas in water is frequently used.

This *hydrogen sulphide water* should be kept in closed flasks protected from the light.[5] In the case of larger apparatus it is prepared by conducting the gas from the generator through washing flasks containing distilled water, or through shallow vessels in which it passes over the surface of water and is kept in constant contact with it. By the use of a device for removing the saturated liquid and simultaneously substituting fresh distilled water, a supply of strong hydrogen sulphide water is always available. (*Cf.* the diagram accompanying the description of Winkler and Kuster's generator, *loc. cit. supra.*)

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[1] *Zeitsch. anal. Chem.*, **21**, 386. *Cf.* also H. Biltz, *ibid.*, **45**, 99.

[2] *J. prakt. Chem.* (*N.F.*), **48**, 595; *Zeitsch. anal. Chem.*, **33**, 584.

[3] *Zeitsch. anal. Chem.*, **33**, 64. [4] *Ibid.*, **41**, 14.

[5] It is advisable to place the hydrogen sulphide water immediately after its preparation in small flasks with a capacity of about 200 c.c., to cork these tightly, and to place them cork downwards in a vessel filled with water to a height of about 10 cm., which is kept in the dark. Otherwise hydrogen sulphide water decomposes with the formation of water and sulphuric acid, and the liberation of free sulphur. In doubtful cases it should be noted whether the liquid still retains a strong odour of hydrogen sulphide and yields a large deposit of sulphur when treated with ferric chloride solution.

Hydrogen sulphide is also used for the laboratory preparation of *ammonium sulphide* and *sodium* (or *potassium*) *sulphide*.

The former is prepared by saturating three parts of aqueous ammonia solution of sp. gr 0·96 with hydrogen sulphide, and then adding two parts of ammonia solution. The resulting colourless liquid contains ammonium monosulphide, $(NH_4)_2S$, together with some ammonium hydrogen sulphide, NH_4SH. By the action of the air it becomes yellow, through the formation of polysulphide

$$2(NH_4)_2S+O+H_2O=(NH_4)_2S_2+2NH_4OH.$$

Polysulphide is also obtained by treating ammonium monosulphide with sulphur.

An analogous method is used in the preparation of sodium (or potassium) sulphide, the alkali hydroxide solution being first saturated with hydrogen sulphide, and an equal quantity of alkali hydroxide solution then added.

Chlorine gas and *chlorine water* must also be prepared in the laboratory.

Eighteen parts of coarse common salt are mixed with 15 parts of finely powdered manganese dioxide, which must be free from calcium carbonate, in a flask into which is then poured a completely cold mixture of 15 parts of about 92 per cent. sulphuric acid of sp. gr. 1·830 to 1·833 and 21 parts of water. On shaking the flask a regular and continuous evolution of chlorine gas soon begins. If it slackens it can be intensified again by gently heating the flask. For the preparation of chlorine water the gas is passed first through a flask containing a little water and then into a flask filled with cold water until the latter is saturated. If chlorine water quite free from bromine is required, the washing flask is changed after about half of the gas has been evolved, and the subsequent gas conducted into a special flask filled with water. For the preparation of chlorine absolutely free from hydrogen chloride, the gas is first passed through a **U**-tube containing fragments of manganese dioxide, or, as proposed by Hampe, through an aqueous solution of potassium permanganate.

Chlorine water must be kept in a cool place and protected from all light, since, without this precaution, it is soon completely decomposed, *i.e.* is converted into hydrochloric acid, while oxygen (from the decomposed water) is liberated. Smaller quantities for use in the laboratory are best kept in a flask which is placed in a cardboard box to protect it from the light, or they may be kept in bottles of black glass.

Chlorine water must have a strong odour of chlorine, and when heated in a porcelain basin should evaporate completely. It should contain little, if any, free hydrochloric acid, so that when shaken with metallic mercury until the odour of chlorine disappears, it should yield a filtrate which is at most faintly acid. On shaking chlorine water with a little carbon bisulphide and finely divided zinc there should not be even a temporary brown-red coloration of the bisulphide (bromine).

A small quantity of chlorine may be readily prepared by causing a mixture of equal parts of hydrochloric acid and water to act slowly and without the aid of heat in a special form of gas generator upon cubes prepared in accordance with Winkler's proposal, by kneading together one part of calcined gypsum and three parts of calcium chloride, until a moist friable mass is obtained.[1]

SEC. 19.

17. Heating Apparatus, and especially Gas Burners.

Gas burners are the most important of the appliances used for producing the heat required by numerous processes (evaporation, distillation, ignition, fusion, etc.) in analytical work. These are all constructed upon the principle devised by Bunsen, and are, therefore, briefly termed *Bunsen burners*.

In many cases they may be replaced by *electric heating appliances* (hot plates, crucible furnaces, etc.), which are based upon the principle that the parts to be heated offer great resistance to the passage of an electric current. They have the advantage that, by a corresponding regulation of the current, the exact temperature desired may be rapidly attained and may be kept constant.

For many purposes, however, especially for the observation of flame tests and the effects of oxidation and reduction processes during heating, the use of heating appliances burning with a flame is indispensable.

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[1] *Zeitsch. anal. Chem.*, **26**, 352.

If illuminating gas is not available, spirit or benzine lamps can be used for all purposes in the place of a Bunsen burner. Apart from the well-known simple spirit-lamp and the *Berzelius* spirit-lamp with introduction of air, both of which are provided with a wick, these lamps depend on the vaporising of the spirit or benzine, and the burning of this gas in the same way as in a Bunsen burner.[1] With regard to such lamps reference may be made to the *Zeitschrift fur analytische Chemie*.

In the place of illuminating gas, water gas, blast furnace gas or air can be utilised; these are conducted through benzine, benzene, and so on, and are thus charged with hydrocarbon vapours (carburetted).

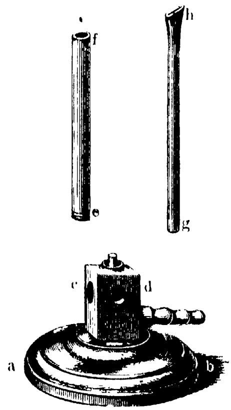

FIG. 21.

Such gases can be burnt in Bunsen burners, but the necessary quantity of air, corresponding to the gas in question, must be carefully regulated, for Bunsen burners depend on the fact that the gas before going through the process of combustion is mixed with a quantity of air scarcely sufficient for complete combustion. The effect of this is that the gas does not burn with a luminous flame at all.

A Bunsen burner consists of the base *ab* (Fig. 21), on which the block (originally square) *cd* rests, which on the one side has holes for the introduction of air, and on the other side has the indented tube for the introduction of the gas inserted into it. This passes inside the block *cd* into a vertical narrow tube, which projects slightly above *cd*. This is closed at the top with a disc, which is provided with three radial slots intersecting at an angle below 60° (in later models with a narrow round opening) for the outlet of the gas in a Bunsen burner. The block *cd* has at the top a screw thread, into which the tube *ef* can be screwed. In this latter the air drawn in by the stream of gas through the side openings in *cd* mixes with gas entering by the central tubes.

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[1] In many cases the sulphur contained in illuminating gas has a disturbing effect, and so evaporating liquids or fused masses which are to be tested for sulphur compounds may absorb sulphur from these compounds, unless they are protected from contact with the gases of the flame.

Fig. 22 shows a Bunsen burner in which the openings for the introduction of air are not in the square block, but in the cylindrical portion which rests on the base. The collar *a* can be screwed higher or lower to regulate the amount of air. The star *cccc* at the top serves as a support for a sheet-iron chimney (indicated by dotted lines).

The Bunsen principle can, of course, be carried out in various forms, *e.g.* in many burners the base has a central opening for the admission of air. For further particulars, see the *Zeitschrift für analytische Chemie.*

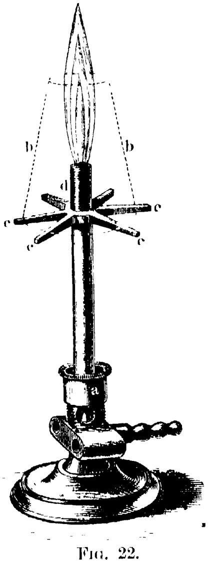

FIG. 22.

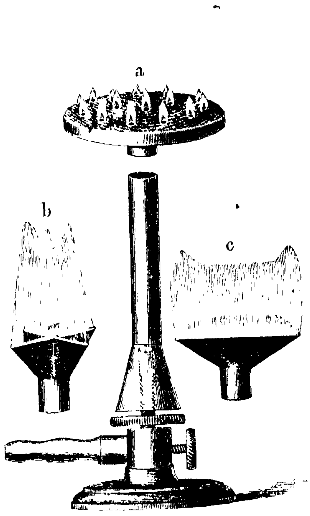

FIG. 23.

Fig. 23 represents a form of burner devised by Teclu,[1] in which the air supply is regulated by screwing up or down the horizontal plate which is just below the lower conical portion of the mixing tube. The gas supply can be regulated by turning the screw opposite the tube for the introduction of gas, so that its conical end acts as a shutter.

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[1] *Zeitsch. anal. Chem.*, **31**, 430.

Various tops can be fixed to the tube according to requirements. In particular, the form marked *b*, which consists of two vertically intersecting slots, is much in use.

In Bunsen burners, when the flame is too low, that is to say, the supply of gas too small, it occasionally strikes back into the tube (the lower gas outlet) so that it burns in the tube, which becomes heated. This can be prevented by reducing the supply of air simultaneously with that of the gas, which can be done in the burners shown in Figs. 22 and 23. This trouble can also be prevented by fixing a small wire netting over the upper outlet of the burner. A constriction of the upper end of the tube has the same effect,[1] for which reason a comparatively large amount of air can be admitted into the Teclu burners.

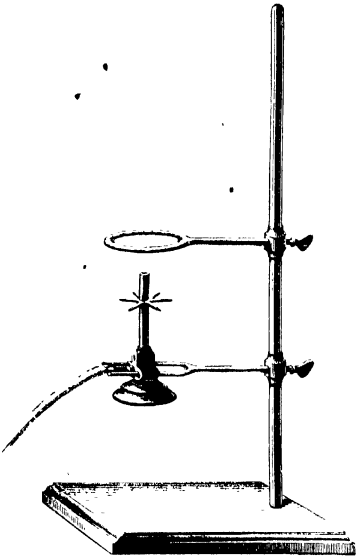

FIG. 24.

If the lamps are to be used for heating flasks, beakers, etc., such glass vessels should be placed on brass wire netting, thin sheet-iron, or asbestos boards. Crucibles and small dishes should be placed on triangles,[2] larger basins directly upon the ring of a tripod or stand.

To derive the full advantage from a flame, it should be at such distance from the article to be heated that the full flame spreads round it.

This can, for instance, be done in the manner shown in Fig. 24, where the lamp and the fork holding it is adjustable on the stand.

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[1] *Cf. Zeitsch. anal. Chem.*, **15**, 314 ; **29**, 576.

[2] For description of these, see Sec. 15, p. 59.

Otherwise the ring on the stand must be adjusted or, in the case of tripods, small blocks of wood placed under the burner.

In particular, when in the case of ignition and fusion a higher temperature is to be reached than is obtainable by simple Bunsen or stronger Teclu burners,[1] bellows should be used, by means of which the combustion of a greater quantity of gas is effected in a relatively small flame by the addition of larger quantities of air, or appliances such as the gas furnaces of W. Hempel [2] and H. Rössler,[3] or an electric crucible furnace.

Apart from purposes of heating, gas burners are also used for producing flame reactions, as already mentioned. To understand them, a more detailed description of the flame of a Bunsen burner is necessary.

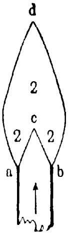

FIG. 25.

We are indebted to the physico-chemical investigations of the last ten years, and particularly to the work of *F. Haber* [4] and his pupils, for a comprehensive insight into the processes of the burning of a Bunsen burner. The main difference between the burning of gas in an ordinary burner and that in a Bunsen burner is that in the latter the necessary air is already to a certain degree mixed with it.

In consequence two distinct combustions take place, one after leaving the burner and the second on the contact of the partly burnt gas with the outside air. If, in order to have accurately defined conditions, we do as Haber did, and take into consideration the flame of a Teclu burner to which a large amount of air is supplied, we find that the first combustion, represented by *abc* in the diagram Fig. 25, takes place in the bright green-coloured zone; the breadth of this zone, which the gas passes in about 0·001 second, is only about 0·1 mm. Its position is determined by the speed of the gas and by the speed of transmission of combustion in the gas.

If the burner is burning properly both velocities are equal, the position of the zone *acb* therefore does not change, it is a question of "steady" combustion. If the velocity of the gas is too small the combustion is transferred to the interior of the tube and the burner strikes back; conversely, the flame may be blown out by a sudden increase in the speed of the gas supply. Fluctuating burning is primarily due to the fact that in short burners there is frequently insufficient mixing of the gases, so that the two velocities previously mentioned are not constant.

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[1] See Terquem burners, *Zeitsch. anal. Chem.*, **20**, 108. As regards other burners with stronger action, see *Zeitsch. anal. Chem.*, generally. Reference may also be made to this journal for Micro-burners.

[2] *Zeitsch. anal. Chem.*, **16**, 454; **18**, 404.

[3] *Ibid.*, **25**, 95; **32**, 593.

[4] *Thermodynamik technischer Gasreaktionen*, p. 282 *et seq.* München, 1905; *Zeitsch. physik. Chem.*, **68**, 726; **81**, 641, and in several other parts of the works mentioned.

The position of the exterior cone *adb* is determined by the fact that the atmospheric oxygen coming from outside is sufficient to cause complete combustion to carbon dioxide and water vapour of the combustible gases coming from the interior.

In the zone *acb*, the inner cone, the air primarily mixed with the gas causes its combustion to a mixture of carbon monoxide, carbon dioxide, hydrogen, and water, which is diluted by the nitrogen of the air.[1] The concentration of the individual constituents of this mixture depend upon the constant K in the equation

$$K = \frac{C_{H_2O} . C_{CO}}{C_{H_2} . C_{CO_2}}$$

the so-called water-gas equation. The equilibrium concentrations C for the individual constituents which are very quickly reached in passing through the inner cone, owing to the acceleration of the reaction which takes place there, remain fairly constant in the whole intermediate region (2) up to the outer cone.

The temperatures in such a flame have recently been very accurately measured, and it has been shown that the temperature of the inner zone of combustion does not reach the degree calculated from the luminosity, but only about 1550°. The characteristic green, or with greater excess of air blue, colour of the inner zone is to be attributed to luminescence phenomena. The hottest part of the flame is immediately in front of the outer zone of combustion (1800°); from that point heating of the gases issuing from the inner combustion zone takes place by conduction and radiation, so that the layers of gas nearest to the external zone of combustion are the hottest. Haber's conclusions are based, as mentioned above, upon a Teclu burner with a plentiful supply of air, such as is also found, outside the laboratory, in the modern *Welsbach* burner and in gas cooking apparatus. By regulating the supply of gas and air different processes may be maintained in the flame, which can be used for oxidation, reduction, fusion, and volatilisation purposes.

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[1] If oxygen is introduced instead of air, a portion of the heat of reaction is not utilised in heating the nitrogen, and the temperatures in the flame become correspondingly higher.

Fig. 26 is a diagram of a Bunsen burner provided with a chimney and an adjustable air-supply. Bunsen has given an accurate description of the characteristics of such a flame. Although his estimations of the temperature conditions have been corrected by Haber's investigations, as already mentioned, his description of the different parts of the flame still holds good.

There are to be distinguished (1) the dark flame cone *aaa'a'*, which contains the cold gas mixed with about 62 per cent. of atmospheric air; (2) the flame mantle *a'ca'b*, which is formed by the burning gas mixed with air; (3) the luminous point *aba*. This, however, is not shown by the normal burner with open air-holes. If it is to be produced, as is necessary in reduction experiments, the air-holes are correspondingly regulated.

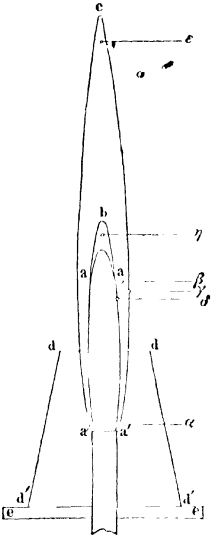

FIG. 26.

In these three main portions of the flame we distinguish, as did Bunsen, six reaction areas (Fig. 26), which were named by him as follows -

1. The *flame basis* at *α*, which is of relatively low temperature, because the gas burning here is chilled by the cold air coming from below, whilst the burner tube also conducts heat away. This part of the flame is frequently used for the detection of readily volatile substances which colour the flame, in the presence of less volatile substances which also colour the flame, since at a relatively low temperature only the former volatilise momentarily, and the resulting fugitive flame colorations appear distinctly and unmixed.

2. The *fusion area*. This is situated at *β*, somewhat above the lower third of the entire height of the flame, equally distant from the outer and inner boundary of the flame mantle, which at this height has reached its maximum width. It is used for testing the fusibility, volatility, and light radiation of substances, and for all fusion processes at a high temperature.

3. The *lower oxidation area* is in the outermost part of the fusion

area at γ, and is particularly suitable for the oxidation of oxides dissolved in glass fluxes.

4. The *upper oxidation area* at ϵ is formed by the upper non-luminous point of the flame. Its action is most powerful when the air-holes of the burner are fully opened. It is used for the removal of volatile oxidation products and for all oxidation processes for which a not very high temperature is required.

5. The *lower reduction area* is at δ, *i.e.* at the inner edge of the fusion area bordering on the dark flame cone. At this point the reducing gases are still mixed with atmospheric oxygen, and therefore do not act with full reducing power, and so leave many substances unaltered which are reduced in the upper flame. This part of the flame is particularly suitable for reductions on carbon sticks (p. 88) and in glass fluxes.

6. The *upper reduction area* is at η in the luminous point which forms above the dark flame cone, when the air-holes are closed to the necessary extent. The restriction of the air-supply must not be carried so far that a test-tube filled with cold water and held in the luminous point becomes coated with soot. This part of the flame contains no free oxygen, is rich in separated incandescent carbon, and has, therefore, a much more pronounced reducing action than the lower reducing area. It is especially used for the reduction of metals, which are to be collected in the form of deposits. Reduction and oxidation processes can best be carried out with the aid of such a gas flame, and by making use of the different parts of the flame.

The investigation of the behaviour of small quantities of solid substances in a flame, such as tests of their fusibility and volatility, the formation of sublimates, the observation of the production of a flame coloration, as also the oxidation and reduction phenomena in the flame produced by them either alone or in admixture with fusion agents, as in the so-called bead reactions, was formerly (*i.e.* before the introduction of the Bunsen burner) carried out exclusively with the aid of a simple spirit lamp, the heat of which was intensified, when necessary, by blowing into it a current of air from a blowpipe, or by means of a luminous flame (candle, etc.) with the aid of the blowpipe.

These tests in the dry way are frequently summarised under the name of *blowpipe tests*. They are still useful in their original form outside the laboratory for the rapid examination of minerals. The use of gas burners, however, when available, is usually preferable.

Bunsen devised a process, described more fully below, in which the blowpipe was not used under any conditions.

We, however, prefer to use the blowpipe for reduction reactions and certain reactions in the oxidising flame, *i.e.* for heating on charcoal, whilst in other cases, for tests in ignition tubes, flame and bead reactions, we recommend the use of a gas flame.

The value of these reactions in the dry way is that they give immediate results. These may either consist in the determination of the properties of the substance under examination, *i.e.* whether it resists the action of heat, is volatile, fusible, etc., or in the appearance of phenomena which enable the particular substance to be immediately identified. Details of individual tests will be found in the outline of preliminary examination in Chapter II.

SEC. 20.

18. Flame Tests, Oxidation and Reduction Reactions in the Flame. Use of the Blowpipe.

To observe the behaviour of substances as regards their fusibility, volatility, and capacity to form a sublimate, small *glass tubes* are used. These are about 7 to 10 cm. long and 5 mm. in diameter, and are closed at one end by fusion.[1] They are prepared by heating the end of the tube in the blowpipe flame until the sides for the length of about 1 cm. have fused together, and then blowing gently into the tube, so as to form a bulb of about 8 mm in diameter. Care must be taken that the walls of the small bulb are as uniform as possible; those in which the glass is thicker in one place will easily crack when subsequently used.

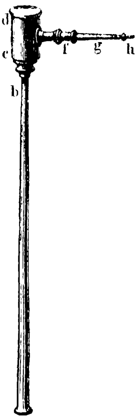

FIG. 27.

The behaviour of the substance in the flame itself is studied either by introducing it into the flame by means of a platinum wire or by heating it on charcoal in the blowpipe flame.

The *blowpipe* (Fig. 27) is a small instrument usually made of brass or German silver. It was first used by metal workers for soldering (by blowing the flame), whence its name. It consists of three separate parts, firstly the tube *ab*, which may be provided with a mouthpiece of horn, through which air is blown from the mouth; secondly, the small cylindrical vessel *cd* (into which *ab* is fixed with an air-tight joint), which serves as an air chamber and collects moisture; and thirdly, the smaller tube *fg*, fixed into *cd* at a right angle and terminating in a finely perforated platinum point, or, better, in a perforated platinum cap *h*, which can be screwed on air-tight. The latter appliance, the details of which are shown in Fig. 28, although somewhat more expensive, is very much more durable than the former. If in time the platinum cap becomes stopped up it can usually be cleared again by ignition.

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[1] *Cf.* Part II., Chapter III., "Notes on preliminary examination." Nos. 1 to 5.

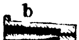

FIG. 28.

The length of the blowpipe must be such that in use the point is plainly visible; it is usually 20 to 25 cm. The mouthpiece varies in form. Some prefer one which is placed between the lips, and others a trumpet-shaped piece against which the lips are pressed. Blowing with the latter is much easier, and this form is, therefore, usually chosen by those who do much work with the blowpipe.

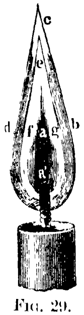

FIG. 29.

The object of the blowpipe is to drive a continuous fine stream of air into (usually) a luminous flame. When the latter burns under normal conditions it will be seen to consist of three parts, which are similar, whether in a candle flame, as shown in Fig 29, or in a gas flame. There is firstly a dark core *aa* in the centre, then a luminous part *efg* surrounding it, and finally a faintly luminous zone *bcd* which surrounds the whole flame. The gases which form the dark core cannot burn for lack of oxygen. In the luminous sphere these gases meet with insufficient air for their complete combustion. Hence it is mainly the hydrogen of the hydrocarbons which burns, while the carbon is separated in a glowing condition and causes the luminosity of this part of the flame. In the outer mantle, however, the supply of air is no longer restricted, so that there combustion takes place of all substances still unburnt. This part of the flame has the highest temperature, and the maximum heat is attained at the extreme point. When oxidisable substances are held in the point of the flame they are very rapidly oxidised, because the necessary conditions of high temperature and free access of air are present. Hence the exterior part of the flame is termed the *oxidising flame*. If, on the other hand, oxidised substances which have a tendency to part with their oxygen are placed in the luminous part of the flame, the opposite conditions hold good, *i.e.* the substances lose their oxygen, which is taken from them by the carbon and still unburnt hydrocarbons in this zone, and are thereby reduced. The luminous part of the flame is therefore termed the *reducing flame.*

When a fine stream of air is introduced into a flame from the side it first alters the form of the flame, which no longer burns straight upwards, but becomes small and pointed in the direction to which it is deflected by the air current, and in the second place it causes combustion to take place not only in the outer zone of the flame, but also within it. Since this has the effect of raising the temperature of the flame considerably, the extremely energetic action of the blowpipe flame can be readily understood. The position of the blowpipe and the manner of blowing must be varied according to whether a *reducing* or *oxidising* action is required.

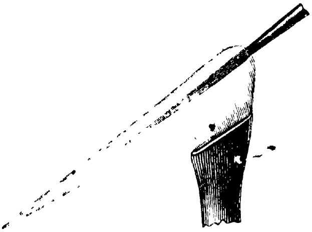

FIG. 30.

The flame is produced either by means of candles, as mentioned above, or especially by means of small paraffin oil or wax lamps with wicks cut at an angle (these wax lamps being heated over a spirit lamp or gas flame until the wax melts, and is then kept fluid by the heat of their own flame), or a luminous gas flame may be obtained by burning the gas without admixture with air in a tube with a flattened top 1 cm long and $1\frac{1}{2}$ to 2 mm. in breadth, which is cut at an angle, as shown in Figs. 30 and 31. Either special gas blowpipe burners may be used, or a slightly narrower tube *gh* (Fig. 21, p. 76) may be

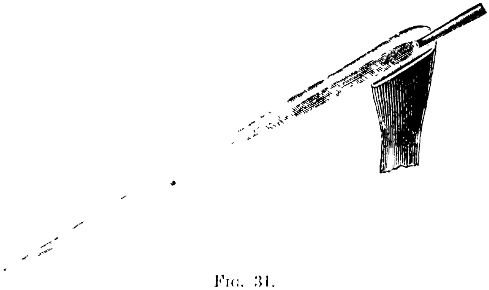

FIG. 31.

placed on the tube of an ordinary Bunsen burner, so as to close the air-holes. The use of gas burners has the advantage that the height of the flame can be regulated. A convenient method of keeping the blowpipe steady is to fix it upon a movable metal support, such as, *e.g.*, the ring of a retort stand.

The flame required for reduction is shown in Fig. 30, that for oxidation in Fig. 31. To produce the *reduction flame* the blowpipe is held in such a way that its point touches the edge of the flame (which must not be too low), and a moderate blast of air is blown into it. Under these conditions there is only an incomplete admixture of air with the gas, and between the inner bluish zone and the outer barely perceptible part of the flame there is left a luminous and reducing zone, the hottest point of which is a little in front of the point of the inner cone of the flame. The *oxidation flame* is obtained by introducing the point of the blowpipe a little further into the flame, which is kept lower than before, and blowing more strongly into it. This causes the air and gas to mix intimately, and there results an only slightly luminous flame cone, surrounded by a narrow pointed pale blue, barely perceptible, mantle.

Blowing must be done only by means of the muscles of the cheeks, and not with the lungs. After a little experience it is not difficult to breathe with the cheeks distended, and, when once this can be done easily with the blowpipe between the lips, only a little practice is required to produce uninterruptedly a steady uniform flame.

Instead of being blown with the mouth, the blowpipe may be attached to a gasometer or small rubber bellows or other constant source of air supply.

Wood charcoal is the material upon which the substance to be tested in the blowpipe flame is generally placed.

The blowpipe is frequently used when it is required to reduce a metallic oxide or the like, or to test the fusibility of a substance. The material under examination is placed in a small shallow hollow scooped in the charcoal by a circular motion with a knife, metal tube (cork borer), etc., or the lower end of the blowpipe *d* (Fig. 27). If the hollow is made too deep the substance to be heated is not brought into proper contact with the flame. Metals which are volatile at the heat of the reducing flame volatilise partially or completely during the reduction. The metallic vapours are burned to oxide again on their way through the outer flame, and this is condensed round the material being tested. When the condensation is pronounced it is termed a deposit. Many deposits have characteristic colours, by means of which the metal can be recognised.

Charcoal selected for this purpose must be well carbonised, since otherwise it will decrepitate and spoil the test. The charcoal of pine, lime, or willow is much better than the charcoal of harder kinds of wood yielding more ash. Smooth pieces are chosen, since parts containing knots decrepitate when heated. The small blocks of wood for the charcoal are preferably sawn from mature, recently cut pine wood in rectangular pieces; if dust is blown from the charcoal it will not soil the hands. Only those sides are used which show the annual growth rings on edge, since on the other sides the fused mass will spread over the surface of the charcoal (Berzelius). Artificially prepared blocks made by compressing wood charcoal powder into suitable shapes are now to be bought, and form a convenient, clean, and excellent substratum for blowpipe tests. Blocks of compressed charcoal, which, owing to the addition of nitre or the like, continue to glow by themselves, are unsuitable for the purpose. The characteristics which make wood charcoal so valuable as a substratum in blowpipe tests are as follows: (1) Its infusibility; (2) its slight heat conductivity, which enables a substance to be heated more strongly on charcoal than on any other substratum; (3) its porosity, which causes readily fusible substances, such as borax, sodium carbonate, etc., to be absorbed, whilst infusible substances remain on the surface; (4) the readiness with which it reduces oxidised substances, so that it assists the reduction of oxides by the inner blowpipe flame.

In testing the behaviour of substances in the flame of a Bunsen burner the material is introduced into the flame with the aid of a *platinum wire*.

Wire of about the thickness of thin piano wire is used for the purpose, one end being fused into a piece of glass tubing as a holder (see Fig. 33, p. 89), whilst the other end is bent into a small loop.

In the case of fusible substances the end of the wire is heated and then dipped into the powdered material, so that it retains a certain proportion of the powder. In testing infusible substances the wire is moistened with water before being dipped into the powder, and the adhering mass slightly dried near the flame before being introduced into it. Decrepitating substances are first ground to as fine a powder as possible, then absorbed by a moistened strip of filter paper with an area of about 1 sq. cm., which is cautiously burned between two rings of fine platinum wire. The substance to be tested is then left as a coherent crust, which can be introduced without difficulty into the flame. Liquids are tested by dipping the loop of platinum wire into them, and evaporating the adherent drop in the vicinity of the flame without allowing it to boil. If platinum wire is attacked by the substance being tested, an asbestos fibre, the thickness of which must not exceed a fourth of that of an ordinary match, may be used.

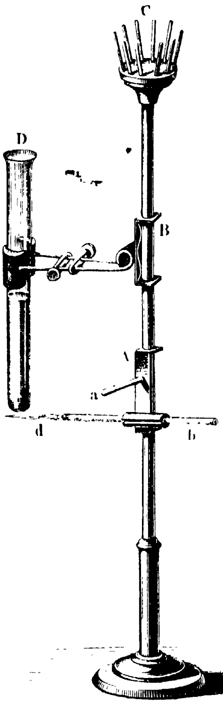

FIG. 32.

If substances are to be exposed to the flame for a longer time, a stand (Fig. 32) is used. The sliding supports *A* and *B* can be readily moved up and down and sideways upon the rod *A* has an arm *a*, upon which is rested the small glass tube into which the platinum wire is fused (Fig. 32), and also a holder for the glass tube *b* with the asbestos fibres *d*. *B* has an arm with a clamp for holding the test-tube, which is to be heated for a considerable time in a definite part of the flame. The uprights on the disc *C* at the top are supports for the glass tubes with platinum wires.

Reduction tests in the flame of the Bunsen burner are made either with suitable reducing agents in small thin-walled glass tubes, or by means of charcoal sticks. (These charcoal stick reactions are a substitute for the blowpipe reduction tests on charcoal.) They are prepared in accordance with Bunsen's suggestion by melting an unweathered crystal of sodium carbonate in the flame, and smearing a wooden match-stick (without its head) for about three-quarters of its length with the resulting semi-solid mass. If the match is then slowly turned round and carbonised in the flame a crust of solid sodium carbonate is formed, which when it is heated in the fusion area of the flame melts and is absorbed by the charcoal. A fragment of the substance under examination (about the size of a small millet seed) is made into a paste with fused sodium carbonate and applied to the end of the charcoal stick, which is to a certain extent prevented from burning away by its sodium carbonate glazing. The point is inserted into the oxidising flame until the mixture melts, and is then passed through a portion of the dark area of the flame into the opposite hottest part of the lower reduction area. The time for the reduction test is indicated by the ebullition of the sodium carbonate. After a few moments the test is interrupted and the substance allowed to cool in the dark core of the flame. Finally, the end of the charcoal stick is scraped off and ground up with water in an agate mortar, so as to obtain the reduced metal in small particles, which, after removal of the charcoal by washing by elutriation, may be submitted to further tests.

Volatile elements capable of reduction from their compounds by means of hydrogen and charcoal may be separated and deposited in elementary form or as oxides upon porcelain The deposited mass is thick in the middle, whilst at the edges it becomes a sort of "bloom" For further identification it may be converted into iodide, sulphide, or other compound These reactions are so sensitive that they can frequently be produced by 0.1 to 1 mgrm.

A metallic deposit is obtained by introducing a pinch of the substance on an asbestos fibre into a not too extensive reducing flame, whilst with the other hand a thin-walled externally glazed porcelain basin, 11 to 12 cm. in diameter, filled with cold water, is held above the asbestos fibre in the upper reducing flame. The metal is thus separated as a dull black or shining deposit.

FIG 33.

If, however, the porcelain dish is held in the upper oxidation area of the flame, deposits of oxides are obtained. In order to ensure their formation when the amount of material is very small, the size of the flame should be correspondingly reduced. By breathing on the dish upon which the deposit of oxide has formed, and placing it in a wide-mouthed vessel, provided with a closely fitting stopper, and containing fuming hydriodic acid, together with some phosphoric acid and melted phosphorus tri-iodide, the deposit of oxide is converted into iodide Should the hydriodic acid have ceased to fume, owing to the withdrawal of water, this property may be restored to it by the addition of a little phosphorus pentoxide. By exposing the iodide deposit to a current of air containing ammonium sulphide and breathing upon it from time to time, and finally removing the excess of ammonium sulphide by gently heating the porcelain dish, the iodide deposit is converted into a deposit of sulphide.

When considerable quantities of reduction deposits are required for further tests the porcelain dish is replaced by a test-tube half full of water (*D* in Fig. 32). The fine asbestos fibres, with the substance attached, are then brought by means of the arm supporting the glass tube *b* into such a position, that they are level with the middle of the upper part of the reducing flame. The arm *B* is then moved, so that the bottom of the test-tube, which it supports, will be directly above the asbestos fibres *d*, and finally the burner is placed below the test-tube. The substance is now introduced into the reducing area, and the metal deposit will be formed upon the bottom of the test-tube, in which some fragments of marble are placed to prevent bumping when the water boils. By repeating the operation a deposit of any desired thickness may be obtained.

SEC. 21.

19. Bead Tests in the Flame.

The reactions obtained in fused glass fluxes constitute a special form of dry tests. If a salt of phosphoric acid (sodium ammonium hydrogen phosphate) or borax is fused in a loop of platinum wire (Fig. 33, p. 89) (and for this purpose a somewhat thicker wire than is there described is preferable), a colourless bead is obtained, and this will dissolve metallic oxides or metallic salts, especially those of volatile acids to produce characteristic coloured fluxes. The colour of these frequently differs, according to whether the mixture was heated in the oxidising or reducing flame. Under certain conditions enamelled opaque beads are obtained or, in the case of silicates, such as are turbid through the separation of silicon dioxide. In making the test the loop of platinum wire is heated to redness and then dipped into the powdered phosphate or borax. The reagent partially melts and remains attached to the wire; and when then heated in the flame, the phosphate froths and loses water and ammonia, and leaves a residue of sodium metaphosphate

$$(NaNH_4HPO_4 = NH_3 + H_2O + NaPO_3).$$

The latter can combine directly with metallic oxides to form orthophosphates, as *e.g.* $CuO + NaPO_3 = CuNaPO_4$. In the case of salts of volatile acids the acid anhydride escapes, and orthophosphate is formed in the bead: $Co(NO_3)_2 + NaPO_3 = CoNaPO_4 + N_2O_5$.

Borax on fusion loses its water. The dehydrated "borax glass," $Na_2B_4O_7$, can also combine directly with oxides or expel anhydrides of volatile acids from their combination in salts, being itself converted into metaborates. Thus, for example:

$$CuO+Na_2B_4O_7=Cu(BO_2)_2+2NaBO_2,$$

$$\text{or}\quad CuCO_3+Na_2B_4O_7=Cu(BO_2)_2+2NaBO_2+CO_2.$$

If gas is not available bead tests may also be made with the aid of a blowpipe and a spirit lamp.

SEC. 22.

20. Observation of Flame Coloration. Spectrum Analysis.

The vapours of many substances emit, in the glowing condition, light of different colours.

In the case of salts the colour usually depends upon the metal present, and is characteristic of it. There are, however, also cases in which the vapours of different salts of the same metal are of different colours, as *e.g.* in the case of the chlorine, bromine, and iodine compounds of copper.

When a small quantity of a volatile compound of such a substance is introduced into a non-luminous flame, it is possible at once to draw a conclusion from the resulting *flame coloration* as to the nature of the substance; in many cases this may be conclusive, whilst in others it affords a definite basis for further deductions.

Thus, for example, sodium compounds impart a yellow coloration, potassium compounds a violet, and lithium compounds a carmine-red coloration to the flame. The flame of a Bunsen burner provided with a chimney is especially suitable for such observations. (*Cf.* Figs. 22 and 26, pp. 77, 81.) The substance to be tested is introduced by means of a small loop in a platinum wire fixed in a suitable holder (Fig. 32, p. 88, or Fig. 34) into the fusion area of the gas flame. The salts of alkali and alkaline earth metals colour the flame to a pronounced extent. On comparing the salts of the same metal it will be found that each salt, provided it is volatile at a high temperature, or at all events allows the metal to volatilise, differs only in the intensity of its coloration, the most volatile producing the greatest effect. Thus, for example, potassium chloride gives a more intense colour than potassium carbonate, and the latter a more intense one than potassium silicate. In some cases the coloration of the flame may be promoted or intensified by the addition of a substance which decomposes the sparingly volatile compound. For example, in the case of silicates, which only contain a small percentage of potassium, that metal cannot be directly detected *by the flame test, but on the addition of a little gypsum the coloration* is produced, owing to the fact that it results in the formation of calcium silicate and of sufficiently volatile potassium sulphate.

But, since the colorations which different substances impart to the flame are sometimes very similar, as, for example, the red colorations produced by lithium and strontium compounds, or the violet colorations produced by potassium, caesium, and rubidium compounds, and since the simultaneous presence of several substances colouring the flame impart a mixed colour, whilst the greater luminosity of one glowing vapour may completely mask the colour of the vapour of another, it is for these reasons frequently impossible to draw any certain conclusion from a simple observation of a flame coloration.

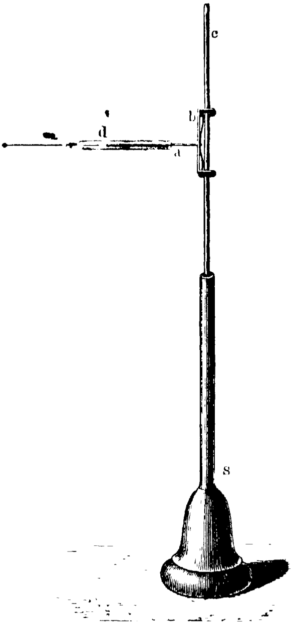

FIG. 34.

This drawback may often be obviated, partially at all events, by observing the flame coloration, not with the naked eye, but through a *light filter*, usually coloured glasses, and by this means absorbing the light produced by certain vapours in a mixture; or the differentiation of the kinds of light emitted by different kinds of vapours simultaneously present may be effected by means of *spectrum analysis*, as described below.

Since the latter method is infinitely superior, all that need be said about the former is that some recommend for use as light filters hollow prisms which have acute angles, and are filled with indigo or potassium permanganate solution, thus allowing the flame to be viewed through any desired thickness of coloured liquid, whilst others have proposed the use of coloured glasses for this purpose.

These consist of a blue, a violet, a red, and a green glass. The blue glass is coloured with cobaltous oxide, the violet with manganic oxide, the red by cuprous oxide, and the green by ferric oxide and cupric oxide. The varieties of glass which can be bought for the decorative treatment of windows are usually of the right shades.

The appearance of the flames coloured by the vapours of different substances when viewed through these screens, and the combinations of screens to be used for the detection of the individual substances, are described in the second part in connection with the corresponding reactions of cations and anions.

Spectrum analysis, the second method for the special observation of flame coloration, is of much greater delicacy and value, and is a physical process of investigation, the fundamental importance of which extends far beyond this particular object.

It is based upon the principle that the light emitted from a source of light, or transmitted through a transparent substance by which it is partially absorbed, is decomposed by means of prisms or gratings into its different fractions, so that the nature and intensity of these can be further investigated. In so far as the nature of the emitted or absorbed light depends upon the chemical composition of the luminous or transparent substance, it is possible to draw exact conclusions as to the constituents of the substance in question from the kinds of light occurring in its spectrum.

Light is produced by electro-magnetic vibrations, the wave lengths of which for the rays visible to the eye vary between 400 and 800 millionths of a millimetre (1 millionth part of a millimetre is written $\mu\mu$). Each vibration of definite wave length produces a definite sensation of colour in our eyes.

In the case of luminous substances the conditions for the rate of transmission of the emitted light rays in different media, *e.g.* air and glass (their refrangibility), vary with the wave length. Hence, in passing through a (glass) prism they are bent (refracted) from their course to a different extent. The longer the wave lengths, the less the refraction of the rays, and *vice versa*. The red rays show the least, and the violet rays the greatest refraction.

When a group of parallel light rays is made to pass through a prism [1] and then received upon a screen or made to enter a telescope tube, the group of rays then produces an image (*spectrum*), in each part of which only light of definite wave lengths (*i.e.* of the same colour) is present.

If the pencil of light contains rays of different refrangibility the spectrum, compared with the original pencil of light, will appear extended and decomposed into the different kinds of light.

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[1] The analogous action of a grating in refracting light need not be described here.

Incandescent solid and *liquid* substances show *continuous* spectra, *i.e.* those which show light of all the possible wave lengths between the two ends of the spectrum, beginning at the red end, and extending, to a degree increasing with the temperature, to the violet end. That is to say, the kind of light emitted by them depends, not upon the substance, but only on the temperature. The appearance is similar to that of the spectrum of the sun, represented in 1 in the table of spectra, except that the dark lines seen in the latter are lacking.

On the other hand, *incandescent gases* or *vapours*, or *rarefied gases*, into which an electric current of high voltage has been discharged, and *fluorescent substances* emit only light of *certain definite wave lengths*, characteristic of the substance in question.

On this account such light shows a spectrum containing several (sometimes very many) lines which, under the same conditions always occur, in the case of one and the same substance, in the same positions in the spectrum, and thus enable that substance to be detected in a luminous body. (*Cf.* Table of Spectra, 2 to 11.) From an observation of the spectrum it is, therefore, also possible to recognise without difficulty each individual in a mixture of substances imparting colour to a flame. Thus, for example, a flame into which a mixture of salts of potassium, sodium, and lithium is introduced shows the complete spectra of the individual metals associated yet distinct.

Each separate line corresponds to a special form of wave motion produced by an electrical particle vibrating in the atom. Hence the study of spectra enables conclusions to be drawn concerning the construction of atoms, analogies to be traced between elements which are also related in other respects, atomic weights to be determined, etc.

In qualitative analysis simple spectroscopes, which allow the whole of the field to be seen at once, are generally used, and they are mainly used for the observation of the bright lines.

Fig. 35 represents a laboratory spectroscope, as designed by Bunsen and Kirchhoff, the founders of spectroscopic analysis.

The prism *P* is clamped to the middle of the plate supported by the stand of the apparatus. The tube *A* has its end away from the prism closed by a plate, in which is a vertical slit, the width of which can be regulated by means of a micrometer screw. The light to be examined (the flame *F*) enters the apparatus through this slit, is rendered parallel by means of a lens at the end of *A* next to the prism, and falls upon *P*. Here it is so deflected that it reaches the telescope *B*, in which the spectrum appears. The tube *C* has its outer end closed with metal foil, in which is cut a horizontal slit.

This tube also has a lens at the end next to the prism, whilst within it, at the focussing point, is a glass plate on which is a photographically reduced millimetre scale. When this is illuminated by a light placed in front of the slit of *C* the prism acts as a mirror, since *B* and *C* are fixed at the same angle with regard to the surfaces of the prism, and an image of this scale is therefore projected into the telescope and in the same plane in which the spectrum lies.

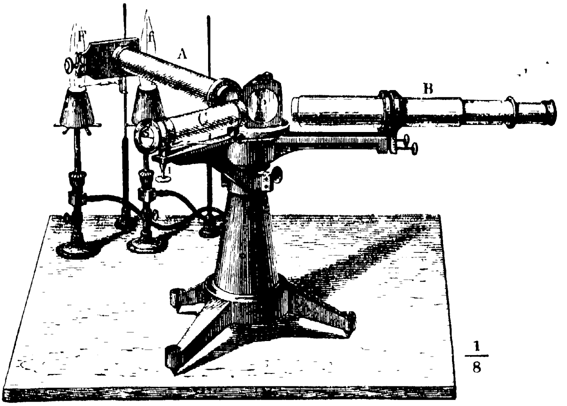

FIG. 35.

If it is required to compare two spectra simultaneously in the apparatus, an appliance (a comparison prism) may be placed in front of the slit of the tube *A* which covers the lower half of the slit, and transmits light by refraction or reflection into the collimator *A* from a source of light at the side.

Spectroscopes with direct vision are more handy for laboratory purposes. The principle used in the construction of these instruments is that instead of a single prism a combination of several prisms of glass of different dispersive power (*i.e.* of colour dissociating capacity) is employed. These prisms are so arranged that light of mean refrangibility passes through them undissociated, whilst rays of short wave length are refracted in one direction, and rays of long wave length in the other. Fig. 36 represents the simplest form of these direct vision instruments, devised by Browning, the so-called pocket spectroscope, the illustration being about two-thirds of the actual size. Behind the opening *g* on the left-hand side is a slit which can be made wider or narrower by turning the projecting studs. The lens, although placed within the limit of vision in front of the ocular opening, brings the image of the slit sharply into the field of vision. *Cr* and *Fl* are prisms of crown and flint glass respectively. The apparatus of Vogel[1] and of Beckmann,[2] which are provided with a number of subsidiary appliances (comparison prisms and a separate tube for the scale), are based upon the same principle.

In the instrument of Bunsen and Kirchhoff, described above, the exact position of rays of definite refrangibility in the spectrum is determined by means of the scale projected from the tube *C*. But different apparatus will only show the same degrees of refraction in the same positions when their prisms have the same refractive and dispersive power, *i.e.* are made of the same kind of glass and have the same angle.

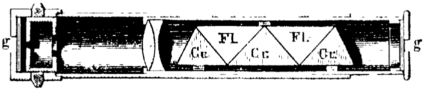

FIG. 36.

The method of indicating the different kinds of rays by their wave lengths is independent of any particular apparatus (or of exact details in the method of employing it). In order to be able to do this from the position of the lines in the scale, it is necessary to standardise the instrument upon wave lengths. For most purposes this may be done by determining the position on the scale of definite lines of known substances, the wave lengths of which are well established.[3] Another method for the orientation of the lines in the spectrum may be used instead of comparison with the scale. For example (as shown in Fig. 55), the light from a flame coloured by the vapours of a known metal may be introduced into the instrument through a comparison prism, which is placed in front of one half of the slit, and the resulting spectrum is compared with that produced by the light entering directly into the other half of the slit, and which

[1] *Ber.*, **10**, 1428; *Zeitsch. anal. Chem.*, **17**, 187.

[2] *Ber.*, **36**, 1984.

[3] *Cf.* Table, p. 97.

is derived from a flame in which the substance under examination is vaporised.

When reflected sunlight is made to pass through the slit of the spectroscope there is produced a continuous spectrum, showing the colours of the rainbow, and in this numerous dark lines may be distinguished (*cf.* 1 in chart of spectra). These dark lines—*Fraunhofer's lines*—occupy definite positions in the spectrum, and hence afford trustworthy points for the orientation of other lines, as, for example, by simultaneously admitting the light from the flame under examination and from reflected sunlight into the two halves of the slit. The explanation of these lines is that the body of the sun in a state of molten heat transmits rays through the solar atmosphere, which produce a continuous spectrum The gaseous substances which compose this atmosphere would themselves produce light spectrum lines, were it not that they absorb from the white sunlight those parts with the same wave lengths as they themselves emit, and thus produce the black lines

The latter, therefore, show exactly the same refrangibility as the bright lines in the spectrum of this vapour. Hence Fraunhofer's lines may be used for standardising the scale of a spectroscope, or for the orientation of the wave lengths of different parts of the spectrum.

The following wave lengths corresponding to the bright lines (or Fraunhofer's lines) of different elements have been determined:

WAVE LENGTHS OF THE ORDINARY KINDS OF LIGHT:—

Potassium α	766·9 $\mu\mu$	red	Hydrogen	α = 656·3 $\mu\mu$			
Lithium α	670·8 ,,			β = 486·1 ,,			
Sodium D_1	589·6 ,,	yellow		γ = 434·0 ,,			
Sodium D_2	589·0 ,,			δ = 410·2 ,,			
Thallium .	535·1 ,,	green	Mercury	615·2 $\mu\mu$	red	491·6 $\mu\mu$	blue
Strontium δ	460·7 ,,	blue		579·0 ,,	yellow	435·9 ,,	
Potassium β	404·1 ,,	violet		576·9 ,,		407·8 ,,	violet
				546·1 ,,	green	404·7 ,,	

FRAUNHOFER'S LINES.

A	Air . . .	760·4 $\mu\mu$	b_1	Magnesium .	517·84 $\mu\mu$
B	Air . . .	686·74 ,,	b_4	Iron . .	516·77 ,,
C	Hydrogen .	656·30 ,,	*F*	Hydrogen .	486·15 ,,
D_1	Sodium . .	589·62 ,,	*G*	Iron . .	430·80 ,,
D_2	Sodium . .	589·02 ,,	*h*	Hydrogen .	410·20 ,,
E	Iron . .	526·97 ,,	*H*	Calcium .	396·86 ,,
			K	Calcium .	393·38 ,,

To obtain the substance under examination in the form of incandescent vapour, the usual method is to proceed as described above in connection with the observation of flame colorations, *i.e.* a small quantity of the substance is introduced on platinum wire into the fusion area of the flame of a Bunsen burner (β in Fig 26, p. 81). Greater luminosity may often be obtained by moistening the substance with a drop of hydrochloric acid, since chlorides are as a rule particularly volatile. Instead of vaporising the substance on platinum wire the method of *E. Beckmann*[1] may be adopted, in which a solution of the substances is converted into fine spray, which is conducted into the flame by means of a current of gas or air. This fine distribution of the liquid is most simply effected by forcing a blast of air through a porous substance in very fine bubbles into the liquid, or by the generation of an inert gas, such as hydrogen and oxygen by electrolysis or hydrogen from zinc and sulphuric acid, in the solution under examination. Figs. 37, 38 and 39 show two forms of Beckmann's "atomiser," in both of which hydrogen is generated in the vessels below the special burners.

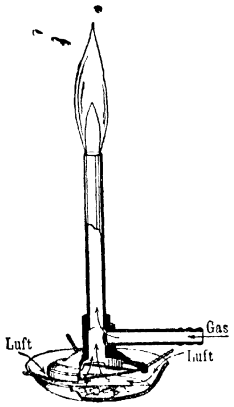

FIG 37.

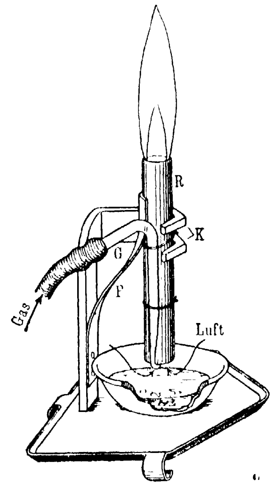

FIG. 38.

For a longer observations of the coloration which the chlorides of heavy metals impart to the flame, one may either adopt the method of *A. Mitscherlich*, in which the metallic chloride is heated in the bulb of a tube drawn out and bent at right angles, while a current of hydrogen is passed through the tube and subsequently ignited; or the apparatus designed by *H. Vogel* for use with ordinary gas, and represented in Fig. 10, may be used.

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[1] *Zeitsch. physiol. Chem.*, 57, 649.

The gas is introduced through *k*, passes through *s* into the glass Bunsen burner *d*, which is supported by the wire *u*, and, if the burner is properly constructed and arranged, burns with a smokeless flame at *a*. On now heating the substance in the tube at *p*, the flame soon shows a lasting coloration corresponding to the chloride present.

In addition to volatilisation in the flame, it is also possible to produce incandescent vapours by volatilisation by means of electric sparks or in an arc light.[1] The spectra of these, corresponding to temperatures different from those in the case of flame spectra, show considerable variations from the latter. In connection with spark spectra reference may be made to the exhaustive communication on the subject by R. Bunsen (*Zeitsch. anal. Chem.*, **15**, 68). It is not possible to give here any description of arc-light spectra, fluorescence spectra, or the spectra of gases, especially those in a rarefied condition, which have received an electric discharge. Further details concerning flame and spark spectra will be found in works dealing specially with the subject, *e.g.* Kayser's *Handbuch der Spektroskopie*, or Emil Baur's *Spektroskopie und Kolorimetrie.*

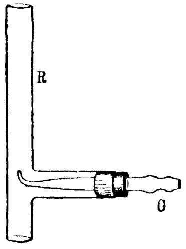

FIG. 39.

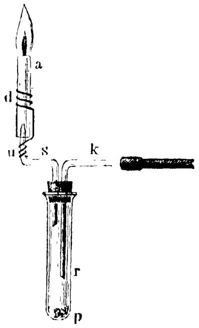

FIG. 40.

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[1] A simple apparatus for the production of arc spectra has been described by Riesenfeld and Pfutzer, *Ber.*, **46**, 37.

Spectrum analysis is not only applicable to the examination of auto-luminous substances, but also affords a means of determining the *absorptive capacity* of transparent coloured substances towards light rays of different refrangibility, and, since this depends upon the composition of the substance, of investigating the latter.

When white light is made to fall upon a colourless transparent substance it is transmitted with uniform brightness as regards all its rays Coloured substances, however, stop the passage of rays of a certain wave length to a varying extent. The transmitted rays no longer unite to form white, but form a mixed colour, the body colour of the substance in question.

If the light from such a coloured transparent substance is decomposed by the prism of a spectroscope into components of different refrangibility, the spectrum when compared with that of white light (*e.g.* sunlight) appears not so bright in certain places This may be manifested in the form of separate narrow lines (as in the case of Fraunhofer's lines or, in fact, of the absorption lines of gases or vapours), or in the form of somewhat faint shadows, which, in the case of the same substance, always appear in the same parts of the spectrum, but vary in intensity with the depth of colour of the substance under examination, or, in the case of coloured solutions, with the concentration. The more distinct and sharply defined the dark stripes, the more readily can a substance be identified by its absorption spectrum. In certain cases (*e.g* the detection of carbon monoxide in blood) an examination of the absorption spectrum is of great importance.

For the examination of their absorption spectra liquids are introduced into vessels with parallel sides, which are placed between the slit of the spectroscope and a strong source of white light

If, on the addition of other substances, solutions show alterations in colour, these may also be followed with the aid of absorption spectrum analysis, which will in this way enable uncoloured substances also to be identified Particulars of this method are given in a detailed communication by *Formanek* upon the detection of metallic salts by means of absorption spectrum analysis with the aid of alkanet (*Zeitsch. anal. Chem.*, **39**, 409).

The special literature must also be consulted in connection with the subject in general. It may be mentioned, however, that *Fritz Weigert*[1] has devised a method of greatly increasing the sharpness of observation of absorption spectra, by determining the brightness for rays of different refrangibility and plotting the results in a curve. This has, in the case of every substance, an absolutely definite form, which can be expressed numerically, so that a more exact objective description of a substance can be given than the statement that its spectrum shows a faint shadow in a definite part of the spectrum.

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[1] *Ber.*, **49**, 1496 ; *Zeitsch anal. Chem.*, **56**, 108.

SEC. 23.

21. Use of the Microscope. Microchemical Methods.

It was stated at the end of Sec 1 (p. 30) that the microscope is frequently used for the examination of small crystals In this way it is frequently possible to identify different substances by the characteristic form of their crystals.

If the microscope is provided with a ruled eyepiece, a stage with circular divisions and two *Nicol* prisms, the angles which the different facets (surfaces) of the crystals form with each other may be measured, and their behaviour in polarised light studied, especially the positions in which the light is obscured in relation to the surfaces of the crystals, etc.

By this means the crystalline form can be ascertained much more accurately (and to some extent expressed numerically) than is possible by simple observation under the microscope. That is to say, more definite and accurate conclusions may be drawn as to the nature of the substance.

An outline of how to use this method, which was originally designed for crystallographic purposes (*i.e.* for the examination of thin sections of rock), for more strictly analytical purposes has been given by J. L. C. Schröder van der Kolk.[1] The same author has also devised a method of determining the refractive index of crystals,[2] which may be used as an additional identification test of the substances themselves.

The microscopic examination of the crystals, which was at one time but little used, has been developed by the work of O. Lehmann,[3] K. Haushofer,[4] A. Streng,[5] H. Behrens,[6]

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[1] *Zeitsch. anal. Chem.*, **37**, 525 *Kurze Anleitung zur mikroskopischen Kristallbestimmung*, published by C. W. Kreidels, Wiesbaden.

[2] *Ibid.*, second enlarged edition, Wiesbaden, 1906; *Zeitsch. anal. Chem.*, **38**, 615.

[3] *Ann. Phys. Chem.* (New series), **13**, 506; *Zeitsch. anal. Chem.*, **21**, 92.

[4] *Mikroskopische Reaktionen*, by K. Haushofer, 1885. (Vieweg und Sohn, Brunswick)

[5] *Ber. Oberhessischen Ges. f. Natur u. Heilkunde*, **22**, 258 *et seq.*; *Zeitsch. anal. Chem.*, **23**, 185.

[6] *Ann. de l'Ecole polyt. de Delft*, 1891; *Zeitsch. anal. Chem.*, **30**, 125 *et seq.*

Frey,[1] Schoorl,[2] Emich,[3] and others, into a definite technique of microscopic investigation, which enables many substances to be identified rapidly, even in the presence of other substances.

The simplest method of applying microchemical reactions is to place a fragment of the substance, together with a drop of water, on an object glass, or to allow a drop of a solution to evaporate on the glass, and in either case to note the form and other properties of the resulting crystals under the microscope.

Not infrequently well-formed crystals are not produced, but only crystalline formations and aggregates, which, however, under the special conditions of their formation are equally characteristic of the substance in question.

Microscopic methods of examination may frequently prove a valuable supplement to the ordinary methods of qualitative analysis, and enable results to be obtained when the usual methods fail; yet they cannot entirely replace the latter, but, on the contrary, in many cases presuppose a knowledge of the ordinary (microchemical) methods.

Moreover, microchemical analysis, if it is to yield trustworthy results, demands not only a thorough knowledge of crystallography, but also skilled practice in the use of the microscope and in microscopical work; it cannot, therefore, taking into consideration the lines upon which it has developed, well be studied at the same time as the purely chemical methods by one who is beginning the study of analytical chemistry. Hence, in the following introduction we have confined ourselves to the description of only such microchemical reactions as are of exceptional value for the identification of certain substances, and as regards the remainder refer the reader to the works cited above. Illustrations of the microscopical appearance of the crystalline substances frequently supplement the description in these books.

Also his introduction to microchemical analysis (5 vols). A new edition of the volume dealing with inorganic compounds has been edited by Kley (1914). This is referred to as Behrens-Kley (3rd ed) in the following pages. The rubric numbers of the volume of the text coincide for the most part with those of the second volume of the edition of Behrens.

[1] *Schweiz. Woch. Pharm.*, **30**, 149; *Zeitsch. anal. Chem.*, **32**, 204.

[2] *Zeitsch. anal Chem.*, **46**, 658; **47**, 209, 367.

[3] *Zeitsch. anal. Chem.*, **42**, 610; **49**, 196; **50**, 500; **54**, 489; **56**, 1; also *Lehrb. der Mikrochemie*, Wiesbaden, 1911 (Kreidel).

SEC. 24.

22. Apparatus and Appliances.

Since many who take up the study of analytical chemistry may find a difficulty in choosing the necessary apparatus and appliances for the purpose, or of deciding which are necessary and which non-essential, we append a list, which gives a brief summary of all the apparatus required for simple examinations, and at the same time take the opportunity of pointing out to what points attention must be paid in buying or making them.

1. A Bunsen gas burner with chimney, support for same, and additional tube for producing a flame suitable for use with a blowpipe, together with a stand (Sec. 17, Figs. 21, 22 and 24)

If gas is not available spirit or petrol lamps are used instead.

2. A blowpipe (*cf.* Sec 20, Fig. 27, p 83)

3. A platinum crucible. It should have a capacity of about 15 c.c., and not be too deep in proportion to its breadth, and its cover should be in the form of a shallow dish In laboratories where several chemists are at work one crucible is sufficient for a number of persons

4. Platinum wire (*cf.* Secs. 20, 21, and 22)

5. A stand with twelve test-tubes, which should be from 16 to 18 cm. in length and 1 to 1.5 cm in width. They must be made of thin colourless glass, and have been cooled in such a way that they do not crack when boiling water is poured into them They should also have round edges somewhat turned over, but no lip, which is of no use for pouring out, and makes it very difficult to close the mouth with a cork or to shake the tube thoroughly. A convenient form of stand is shown in Fig 11 The pegs on the upper shelf support the rinsed test-tubes, which are thus drained and are dry when required.

6. A few beakers and boiling flasks made of fairly thin glass which has been properly, *i.e.* slowly, cooled

7. Some porcelain basins and a selection of small porcelain crucibles.

8. Glass funnels of different sizes They should be inclined at an angle of 60°, the sides not passing gradually into the outlet tube, but being connected with it at an acute angle.

9. A washing bottle, holding about 300 to 400 c.c. (See Fig. 5, Sec. 8, p 41)

10. Some glass rods, a glass spatula, and assorted pieces of glass

tubing. The latter are drawn out, bent, etc., over the gas flame, whilst the ends of the former are rounded by fusion. In cutting glass tubing into the desired lengths a mark is made with a moist three-cornered file at the place in question, the tube grasped with one hand to the right and the other to the left of the scratch, and then snapped in two. The non-luminous flame of a Bunsen burner or blowpipe flame is used for fusing and drawing out tubing, but for bending it a broad luminous flame is preferable.

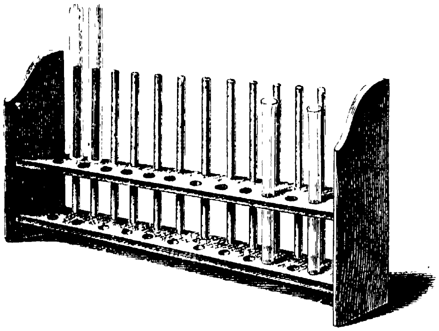

FIG. 11.

11. Several clock glasses.

12. A small porcelain or agate mortar.

13. Crucible tongs of brass or steel, 10 to 12 cm. long.

14. A filter stand, Fig 1 or 2, p 37.

15. A tripod of thin iron to support dishes, etc., when being heated over a gas burner.

16. Wire gauze or asbestos board, p. 78.

17. A triangle of platinum wire or of iron wire, covered with unglazed porcelain or quartz glass Figs. 16 and 17, p. 59.

18. Coloured glasses, especially a green and a blue one, as described on p. 92

19. A pipette delivering 10 c.c , graduated in 0·5 c.c.

20. Filter paper or ready-made filters.

CHAPTER II.

BEHAVIOUR OF SUBSTANCES TO REAGENTS.

In this chapter we shall discuss in detail the characteristic properties and phenomena which individual substances reveal under certain conditions, especially in interaction with other substances, whereby their presence can be recognised. Such phenomena are termed reactions, the substances used for their production reagents (See p. 7.)

Before describing the individual reactions we give, firstly, a general description of the reagents and their application; and secondly, an outline of the meaning and nature of reactions and also of the system of analytical grouping.

SEC. 25.

I. REAGENTS AND THEIR APPLICATION

As mentioned above, the chemical action of different substances on one another is termed "Reaction." If the phenomena which arise enable a definite substance to be recognised, it is called a *reaction of this substance.* For example, if one knows that solutions of barium salts treated with sulphuric acid yield a white precipitate insoluble in acids, and, on the addition of a solution containing barium ion to a liquid under examination, a precipitate is obtained with the above-mentioned properties, the conclusion may be drawn that sulphuric acid (sulphate ion) is present in the solution. Substances which are used in the examination of other substances to produce a reaction are called *reagents.* They may be divided into two classes, *general* and *special.* The former are used to determine the class or group to which the substance under examination belongs, the latter to identify definite individual substances.

The dividing line between these general or group reagents and the special reagents is difficult to define, as a reagent occasionally serves both purposes.

If, however, we make the distinction, it is in order to show that in each case the object for which the reagent is to be used must be clearly understood.

The value of *general reagents* is that it enables analytical groups to be sharply defined and, in many cases, the substances belonging to one group to be separated from those belonging to another. On the other hand, it is essential for *special* reagents to be *characteristic* of special substances, and to be *sensitive*. A reagent is characteristic when the phenomenon arising through its application is only produced by the special substance for the determination of which it is used, so that a wrong conclusion cannot be drawn. Iron is thus a characteristic reagent for copper, stannous chloride for mercury, because the metallic copper (mercury globules) obtained in these reactions cannot be confused with other substances.

A reagent is sensitive when its action is distinct, even when the minutest quantity of the substance to be ascertained is present, *e.g.* starch upon iodine. Many reagents are both characteristic and sensitive, as, for example, aurohydrochloric acid for stannous ion, potassium ferrocyanide for ferrous and cupric ions, etc.

In the *use of reagents* it is essential to know the conditions which must be observed in order to ensure their correct action; that is to say, to be able to draw trustworthy conclusions from the appearance or non-appearance of the reactions.

In the first place it is necessary for the reagent to be pure, so that misleading side-phenomena do not arise owing to the presence of foreign substances. Reagents should, therefore, be tested for purity before use, and be protected from contamination before and during use.

It should be a habit, for instance, to take strict care that the stoppers of bottles containing reagents are neither interchanged nor laid on the laboratory bench with the ground surface downwards; it is advisable to use stoppers with a broad flat top, and to place them top downwards on the bench. The edge of the neck of the bottle should always be wiped out with filter paper before the reagent is poured out, in case some of the reagent may have dried on it, or some of the ammonium salts from the air or dust may have accumulated there. Care should also be taken when pouring a liquid into a vessel containing gases or vapours (hydrogen sulphide, hydrochloric acid, ammonia, etc.) that these do not penetrate into the reagent bottle and mix with the reagent. In such a case the requisite quantity of fluid reagent should be poured into another vessel first, and from this into that containing gas or vapour.

The possibility of *changes* in the reagent while being kept must also be taken into consideration. Solutions of sodium hydroxide, ammonia, and ammonium sulphide can absorb carbon dioxide from the air; as a result of oxidation by atmospheric oxygen ammonium sulphide may contain sulphate, the gases may escape from aqueous solutions of hydrogen sulphide, sulphur dioxide, and chlorine, or these solutions may become oxidised or decomposed (see p. 73, footnote, and p. 74); aqueous solutions of alkaline substances may attack the glass of the bottle and absorb aluminium or silicate ion, and so forth. Reagents, therefore, which were found to be pure when tested may later be found to have become impure. If unexpected phenomena occur an examination of the reagents should always be made as to whether they have become impure or have changed.

Most reagents can be bought nowadays made up in sufficiently pure condition. Directions for their preparation are, therefore, only given in this book when it must take place in the laboratory. In respect hereof, reference should be made to the foregoing sections, notably Sec. 12, p. 52, Sec. 18, p. 67 *et seq.*, as also to the directions given in special cases later on.

Details for testing the purity of reagents are only given in special cases. We recommend, however, the special book on this subject: *Die Prufung der chemischen Reagenzien auf Reinheit*, which is published by the firm E. Merck, in Darmstadt, and which contains all the necessary directions.[1] Generally speaking, any one who is conversant with qualitative analysis can easily determine the state of purity required for individual reagents and the method of testing them in certain cases, especially when the purpose of their use and consequently the impurities which would be detrimental are borne in mind.

Apart from the question of purity, it is essential for reagents to be used under *the proper conditions*. The first consideration is the *quantity*, then the *dilution*, the *temperature*, and finally the *duration of action*.

In this respect the following remarks are applicable: A wrong proportion of the constituents, *i.e.* an incorrect quantity of reagent added to a substance under examination, is one of the most customary sources of failure in qualitative analysis. Expressions such as an addition in excess, supersaturation, and many others are apt to mislead the student to the assumption that too much reagent cannot be added, and in order not to use too small a quantity many pour out a whole test-tube full of acid to neutralise a few drops of an alkaline liquid, whereas each drop of acid which is added after the point of neutrality has been reached must be considered as an excess of acid.[1] In the same way, too small an addition must be avoided as much as too large a one, in that the use of an insufficient quantity of reagent will often produce quite different phenomena from those obtained from an excess For example, mercuric chloride gives a white precipitate on the addition of too little, and a black one on that of too much hydrogen sulphide. From experience it can be said that beginners generally render their work more difficult and unreliable because they use reagents in too large quantities.

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[1] With regard to reagents for microchemical analysis, see Behrens-Kley: *Mikrochemische Analyse*, 3rd ed., p. 20; W. Lenz: *Zeitsch. anal. Chem.*, 52, 90.

One reason why an excess in the quantity of the reagent used is a mistake is that too great an increase of volume diminishes the sensitiveness of the reactions, and frequently prevents phenomena, which would have occurred had the addition been suitable, from being observed at all. Secondly, it should be noted that the excess of a reagent often disturbs the original reaction (a precipitate obtained dissolves again, etc).

With regard to the adequate *dilution* of solutions of reagents, it should be noted that, as, for instance, in the case of precipitation reactions, the solubility product (see p. 33) is already exceeded by an addition of a solution of reagent, which is smaller in proportion as the solution is more concentrated, and therefore too dilute a solution can in some cases never bring about a precipitation. Reagents which, on the other hand, are too concentrated often produce too dense a precipitate, which can then (by mechanical enclosure or adsorption) easily carry with it foreign particles from the solution, from which even by washing it is difficult to separate it. In such cases it is also often difficult to recognise the nature of the precipitate (*i.e.* whether it is pulverulent, flocculent, crystalline, etc).

As regards the quantities required to cause a reaction, a quarter to a third of a test-tube of prepared solution for each reaction may, as a rule, be used, unless a different quantity is specified for an individual case. A piece about the size of a pea should be used in the case of solid substances, this being dissolved in a quarter to a third of a test-tube of solvent.

No general rules can be given regarding the correct *temperature* and the *duration of action*.

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[1] Sufficient emphasis cannot be laid on the necessity of always using test paper.

On the whole, as regards the observation of proper conditions in the use of reagents, no special rules can be made, but *a general* rule will, in most cases, suffice to produce the correct proportion, or, in other words, the correct conditions It is this, that every time a reagent is applied, the purpose for which it is being used should be clearly thought out, as also the phenomena which it is desired to obtain and the results which the addition of an excess, *i.e* the use of a reagent under unsuitable conditions, would produce.

In *measuring* the quantities of reagents to be used in individual cases, it is necessary to know the *concentration* of their solutions

This concentration can either be measured by making a solution of each reagent of suitable strength for the customary method of use, without there being a reciprocal relationship between the volumes of the individual solutions; or by using solutions of such strength that equal volumes contain corresponding quantities of dissolved substances (thus, for instance, equal volumes of acid and alkali solution neutralise each other, equal volumes of a solution of a barium compound and a sulphate precipitate each other reciprocally, etc); or finally, by taking the middle course, whereby although equal parts of the solution do not contain corresponding quantities there is a known relationship between the volumes of the different solutions (thus 1 part of the one corresponds to 2 parts of the second or 5 parts of the third).

The first method is the one most in use, and we have adhered to it in this book, and at the end of this section have given a summary of the concentrations of the customary solutions of reagents

The second method consists, for example, in the plan of using throughout solutions of reagents of so-called double normal concentration, *i.e.* solutions which contain a quantity of reagent corresponding to 2-gramme equivalents per litre. (An equivalent weight is the quantity corresponding to one effective valency, thus 1 molecule of sodium hydroxide, NaOH, $\frac{1}{2}$ molecule of barium hydroxide, $\frac{Ba(OH)_2}{2}$, 1 molecule of hydrochloric acid, HCl, $\frac{1}{2}$ molecule of sulphuric acid, $\frac{H_2SO_4}{2}$, 1 molecule of sodium chloride, NaCl, $\frac{1}{2}$ molecule of sodium sulphate, $\frac{Na_2SO_4}{2}$, etc. A gramme equivalent is the number of grammes corresponding to these equivalent weights.)

This system has the drawback, that many solutions are too dilute and others too concentrated for the purpose in question.

The third method of measuring the concentration originated with

Wollny (*Zeitsch. anal. Chem.*, **24**, 402). According to this method, normal, five times normal, ten times normal, etc., solutions are used; the degree of normality must in this case be stated on the bottles. Wollny recommends that reagents be taken from the bottles by means of small pipettes, and that in each case a known number of cubic centimetres be used.

We now give a summary of the concentration of the customary solutions of reagents according to the first method, on which the directions in this book are based, and in certain cases add a few special remarks.

A. Acids.

1. Fuming **hydrochloric acid** of sp. gr. 1·19 contains 37% HCl
   Concentrated ,, ,, ,, 1·17 ,, 32% HCl
   Dilute ,, ,, ,, 1·12 ,, 25% HCl
2. Fuming **nitric acid** of sp. gr. . 1·47–1·5 ,, 83–86% HNO_3
   Concentrated ,, ,, . 1·40 ,, 65% HNO_3
   Dilute ,, ,, . 1·20 ,, 33% HNO_3
3. Concentrated **Sulphuric acid** of sp. gr. 1·84 ,, 95–96% H_2SO_4
   Dilute ,, ,, ,, 1·11 ,, 16% H_2SO_4
4. **Acetic acid** of sp. gr. . . 1·040–1·042 ,, abt. 30% CH_3COOH

B. Hydroxide Solutions.

1. **Sodium hydroxide solution** of sp. gr. 1·13–1·15 contains 11–13 per cent. NaOH. Especially when kept for some time in a glass bottle it is never free from aluminium ion, silicate ion, and carbonate ion, and even otherwise not always free from impurities. In many cases it is therefore advisable immediately before use to prepare an alkali hydroxide solution of pure solid potassium or sodium hydroxide (that prepared from metal is especially pure).

Sodium hydroxide solution keeps better in nickel flasks than in glass bottles. As glass stoppers become so firmly fixed in the neck of bottles containing sodium hydroxide solution, if kept for some time, that they cannot be removed, rubber or nickel stoppers may be used. This difficulty can also be overcome by smearing the glass stopper with paraffin wax before inserting it into the neck of the bottle, which should be wiped out first. Another method is to use a cap, which fits tightly round the outside of the neck of the bottle, instead of a glass stopper.

2. **Ammonia** of sp. gr. 0·96 contains 10 per cent. NH_3. It easily

absorbs carbon dioxide or hydrochloric acid and possibly nitric acid from the laboratory air, and must, therefore, be protected from it, and in the event of unexpected reactions appearing should be tested for such impurities

3. **Baryta water** contains 5 per cent. $Ba(OH)_2 + 8H_2O$.

4. **Lime water** contains 1·5 per cent. $Ca(OH)_2$.

Baryta water and lime water absorb carbon dioxide from the air, and barium or calcium carbonates separate, so that the clear solutions (filtered if necessary) are free from carbonate. Lime water, weak in itself, can in this way easily lose its entire content of calcium hydroxide. In many instances *milk of lime*, a mixture of lime water and solid calcium hydroxide, is used. Milk of lime is made by slaking pure quicklime with a fair amount of water, lime water by pouring off the supernatant clear liquid produced when the dilute milk of lime has subsided.

C. Salt Solutions.

The following quantities of water are used to make the customary solutions:—

1. **Ammonium chloride,** 1 part NH_4Cl . . . 8 parts water.

2. **Ammonium carbonate,** 1 part $(NH_4)_2CO_3$, 1 part ammonia and . . . . . 4 ,, ,,

The solid ammonium carbonate as purchased is a mixture of ammonium carbamate and ammonium hydrogen carbonate; to convert this into ammonium carbonate a little ammonia should be added during the solution (an excess does no harm).

3. **Ammonium oxalate,** 1 part $(NH_4)_2C_2O_4 + H_2O$ . . . . . . 24 parts water

4. **Ammonium molybdate,** $(NH_4)_6Mo_7O_{24} + 4H_2O$: 150 gr. of the salt are dissolved in 1 litre of water, the solution poured into 1 litre of nitric acid of sp. gr. 1·2, the fluid allowed to stand for several days in a warm place, poured off from any ammonium phosphomolybdate which may have formed, and then kept for use.

5. **Disodium hydrogen phosphate,** 1 part $Na_2HPO_4 + 12H_2O$ or sodium ammonium hydrogen phosphate $Na(NH_4)HPO_4 + 4H_2O$ . . . 10 parts water.

6. **Sodium carbonate,** 1 part Na_2CO_3 or 2·7 parts crystallised soda $Na_2CO_3 + 10H_2O$ . . . . . . 5 ,, ,,

7. **Sodium acetate,** 1 part $CH_3 \cdot COONa + 2H_2O$ . . . . 10 parts water

8. **Potassium sulphate,** 1 part K_2SO_4 . 12 ,, ,,

9. **Potassium nitrite,** 1 part KNO_2 . 2 ,, ,,

The solution must yield a large quantity of nitric oxide gas on the addition of dilute sulphuric acid.

10. **Potassium chromate,** 1 part K_2CrO_4 . 10 parts water.

11. **Dipotassium dihydrogen pyroantimonate,** 1 part $K_2H_2Sb_2O_7 + 6H_2O$ about 250 ,, ,,

1 part should be boiled for a short time with 200 parts of water, allowed to cool, and the still undissolved residue filtered off.

12. **Potassium cyanide,** 1 part KCN . 4 parts water.

The solution is prepared just before use.

13. **Potassium ferrocyanide,** 1 part $K_4Fe(CN)_6$ . . . . . . 12 ,, ,,

14. **Potassium thiocyanate,** 1 part $KCNS$ 10 ,, ,,

15. **Barium chloride,** 1 part $BaCl_2 + 2H_2O$ 10 ,, ,,

16. **Barium nitrate,** 1 part $Ba(NO_3)_2$. 15 ,, ,,

17. **Calcium chloride,** 1 part $CaCl_2 + 6H_2O$ 5 ,, ,,

18. **Calcium sulphate,** $CaSO_4 + 2H_2O$. Saturated solution

19. **Magnesium sulphate,** 1 part $MgSO_4 + 7H_2O$ . . . . 10 parts water.

20. **Ferric chloride,** 1 part $FeCl_3$ . . 7·5 ,, ,,

21. **Cobaltous nitrate,** $Co(NO_3)_2 + 6H_2O$ 10 ,, ,,

22. **Silver nitrate,** 1 part $AgNO_3$ . . 20 ,, ,,

23. **Lead acetate** (sugar of lead), 1 part $(CH_3COO)_2Pb + 3H_2O$ . . . 10 ,, ,,

24. **Mercurous nitrate,** $Hg_2(NO_3)_2 + 2H_2O$.

The crystals are dissolved by grinding them in a mortar with water to which $\frac{1}{16}$ nitric acid of sp. gr 1·2 has been added The solution is kept in a bottle, which has a little metallic mercury at the bottom.

25. **Mercuric chloride,** 1 part $HgCl_2$. 16 parts water

26. **Cupric sulphate,** 1 part $CuSO_4 + 5H_2O$ 10 ,, ,,

27. **Stannous chloride,** 1 part $SnCl_2 + 2H_2O$

Powdered tin is dissolved by boiling in concentrated hydrochloric acid (tin must remain in excess) until scarcely any more hydrogen is liberated, and the liquid is then diluted with four times its volume of water to which a little hydrochloric acid has been added, and filtered. The solution is kept in a bottle containing some metallic tin (a sheet of tin foil).

28. **Aurohydrochloric acid** (gold chloride),
1 part $HAuCl_4 + 3H_2O$ . . . 30 parts water.
29. **Platinohydrochloric acid,** 1 part
$H_2PtCl_6 + 6H_2O$ . . . . . 10 ,, ,,

SEC. 26.

II. THE NATURE AND SIGNIFICANCE OF ANALYTICAL REACTIONS AND THE SYSTEM OF ANALYTICAL GROUPING.

As explained in the Introduction, the object of qualitative analysis is to identify the chemical nature of substances, whether alone or in association with other substances, in the material under examination. This identification may be at once effected either by the observation of certain definite characteristic properties (colour, crystalline form, etc.), or by placing the substance under such conditions as will cause it to undergo alterations, the kind and course of which depend upon the chemical nature of the substance, are characteristic of it, and so may be used for its identification.

Such alterations may be of either a physical or chemical nature. When they are produced by a second substance acting upon that under examination a chemical reaction is present. The substance used to produce it is a reagent. In its widest significance the term *reaction* is also applied to those phenomena (appearing without the application of reagents) which are used for the identification of substances. These are, therefore, included in the following pages.

In the majority of cases not elements but chemical compounds are present, and the solutions of all of these which contain the same cation invariably show a large number of reactions in common, irrespective of what the anion is in the solution. In like manner, substances whose solutions contain the same anion show a whole series of similar reactions (see Sec. 21).

Again, in the case of metals which can show different valencies (and the solutions of which therefore contain different ions), or which are able to form complex ions, there are separate characteristic reaction groups for each series of compounds whose solutions contain the same ions. For example, ferrous, ferric, ferrocyanide, and ferricyanide compounds all show different kinds of reactions.

In an analogous manner the different compounds of the same metalloid, the solutions of which contain the same anions, are also always characterised by a group of similar reactions, *e.g.* the sulphides, sulphites, and sulphates.

Since, in accordance with the theory outlined on p. 21, ions may be assumed to be the constituents of chemical compounds even in the molecules, the reactions described in the following pages always refer to the ions, even when it is a question of reactions which concern the undissociated salt of the particular ion.

In order to *identify* an ion by its reactions it is necessary to have a *knowledge* of these, that is to say, it is necessary to know *which* reactions under definite conditions indicate the presence of *this* ion, and the conditions under which the reactions take place. Hence, before applying the distinctive methods of qualitative analysis to unknown substances, it is necessary to become acquainted with the reactions of the individual ions.

It requires practical training for the student to become thoroughly acquainted with the peculiarities of phenomena and the production of the conditions which cause them to occur, because neither of them can be adequately explained by a description alone, whilst, on the other hand, a full grasp of the numerous individual reactions is not possible without a clear understanding of the chemical processes, and the arrangement of the reactions in a definite system, which facilitates a general survey and brings into prominence the similarities or dissimilarities of different classes of substances. For this reason the contents of the following chapter must not only be studied, but also be tested by practical work in the laboratory.

The necessary general survey of the reactions is attained by arranging the substances, the ions of which show analogies in many respects, in groups, so that, on the one hand, the similarity of the members of one group with regard to a series of reactions is shown, as compared with the behaviour of the members of another group, whilst, on the other hand, the differences between the individual members of a group may be recognised.

This classification, in accordance with the properties of value for analysis, is the initial stage in the systematic grouping of the elements, and is thus a forerunner of the very comprehensive *periodic system of the elements*. This consists of an arrangement of the elements in the ascending order of their atomic weights, and a grouping of them into periods (see adjoining table). This has the result that the elements in the vertical series of the arrangement show far-reaching analogies in their properties. But there are also in the horizontal series quite definite co-ordinated relationships. Hence it is possible from the position of an element in the periodic system to predict its density, melting-point, etc., and, in short, its physical behaviour, as

PERIODIC SYSTEM OF THE ELEMENTS (ABRIDGED FORM, AFTER BRAUNER).

The numbers in brackets show the analytical groups according to cations

Group	0	I	II	III	IV	V	VI	VII	VIII	
Series					RH_4	RH_3	RH_2	RH		
	R	R_2O	R_2O_2	R_2O_3	R_2O_4	R_2O_5	R_2O_6	R_2O_7	R_2O_8, R_2O_6, R_2O_4 R_2O_3	Intermediate forms of combination
1	—	H 1·008	—	—	—	—	—	—	—	
2	He 4·0	Li 6·94 (I.)	Be 9·1 (III.)	B 11·0	C 12·005	N 14·01	O 16·00	F 19·0	First small period.	
3	Ne 20·2	23·00 Na (I.)	24·32 Mg (II.)	27·1 Al (III.)	28·3 Si	31·04 P	32·06 S	35·46 Cl	Second small period.	
4	Ar 39·88	K 39·10 (I.)	Ca 40·07 (II.)	Sc 44·1 (III.)	Ti 48·1 (III.)	V 51·0 (IV.)	Cr 52·0 (III.)	Mn 54·93 (IV.)	Fe 55·84 (IV.) Co 58·97 (IV.) Ni 58·68 (IV.)	(Cu 63·57) (V.)
5	—	63·57 Cu (V.)	65·37 Zn (IV.)	69·9 Ga (IV.)	72·5 Ge (VI.)	74·96 As (VI.)	79·2 Se (VI.)	79·92 Br	First great period.	
6	Kr 82·92	Rb 85·45 (I.)	Sr 87·63 (II.)	Y 88·7 (III.)	Zr 90·6 (III.)	Nb 93·5 (III.)	Mo (VI.)	—	Ru 101·7 (V.) Rh 102·9 (V.) Pd 106·7 (V.)	(Ag. 107·88) (V.)
7	—	107·88 Ag (V.)	112·4 Cd (V.)	114·8 In (IV.)	118·7 Sn (VI.)	120·2 Sb (VI.)	127·5 Te (VI.)	126·92 I	Second great period.	
8	Xe 130·2	Cs 132·81 (I.)	Ba 137·37 (II.)	La 139·0 (III.), etc.[1]	Ce 140·25 (III.)	Ta 181·5 (III.)	W 184·0 (VI.)	—	Os 190·9 (V.) Ir 193·1 (VI.) Pt 195·2 (VI.)	(Au 197·2) (VI.)
9	—	197·2 Au (VI.)	200·6 Hg (V.)	204 Pl (IV.)	207·20 Pb (V.)	208·0 Bi (V.)	—	—	Third great period.	
10	—	—	Ra 226·0 (II.)	—	Th 232·4 (III.)	—	U 238·2 (IV.)	—	—	
11	—	—	—	—	—	—	—	—	Fourth great period	

---

[1] Elements of the rare earths, all in analytical Group III:

Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
140·6	144·3	150·4	152	158·3	159·2	162·5	163·5	167·7	168·5	173·5	175·0

also its valency, its reactions, and its chemical behaviour Speaking generally, this relationship may be expressed as follows: The properties of the elements are periodic functions of their atomic weights.

From this the conclusion might be drawn that the system of analytical groups coincides with the periodic system, or is so far included therein, that it can be directly deduced from the latter (as the more comprehensive scheme). This, however is only partially the case.

Whereas in the *periodic* system the *total* characteristics of the different elements are taken into consideration, in the *analytical* system the chief value is assigned to the differentiation of differences of behaviour in respect of *one* property to which possibly a subsidiary position is given in the periodic system, as, for example, the finer distinctions in the solubility of the sulphides in the case of the groups with higher cations [1]

In any case, it is not sufficient to take into consideration only the analogies which occur in the vertical series, but attention must also be paid to the similarities and gradational stages which appear in the horizontal series, and especially in the great periods.

There is no doubt but that in a more extended amplification of the significance of the grouping of the elements in the periodic system it will be possible to discover a still closer agreement with the classification into analytical groups.

In order to show the similarities and dissimilarities which have been observed, the *analytical groups of cations* are indicated by a Roman numeral, below the usual arrangement of the periodic system, in the preceding table of the elements.

In the case of the anions, the recognition of the correspondence between the members of the same analytical groups and the position of the respective metalloids in the periodic system is rendered more difficult by the fact that it is a question partly of elements occurring in an uncombined condition, and partly of groups of a metalloid with more or less oxygen atoms. Apart from that, the grouping of the anions is not so important from an analytical point of view as in the case of the cations.

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[1] With regard to the relationship between the properties of analytical importance of the sulphides and the position of the elements in question in the periodic system (and in their order of tension), *cf.* Schurman, *Liebig's Ann.*, **249**, 326; Bodlander, *Zeitsch. physiol. Chem.*, **27**, 55; O. Weigel, *ibid.*, **55**, 293; O. Brunner and S. Zawadzki, *Zeitsch. anorgan. Chem.*, **65**, 136; **67**, 454, where further references are given. See also Part II., chap. iii., No. 18.

In the following survey of the assignment of the different metals to the groups of the analytical system we have arranged the elements within each of these groups in the order of their ascending atomic weight (as in the periodic system).

In the subsequent treatment of their behaviour towards reagents we have, for didactic reasons, chosen a somewhat different order of arrangement, on the one hand, by separating the more important elements and those of more frequent occurrence from the rarer elements, which need not be studied at first; and, on the other hand, by giving prominence, as a rule, to the reactions which effect the sharpest distinction between the members of an analytical group. One result of this, for example, has been the arrangement of the elements in the first two groups in the order of descending atomic weights This appeared to us more suitable, however, than by dealing directly, in the case of both groups, with the behaviour of reagents towards elements with which they produced *no* precipitates, and thus making a beginner commit to memory the cases in which a phenomenon did *not* occur, while only subsequently learning to recognise these elements in their characteristic forms. Apart from this, elements are frequently grouped in an order other than that of their ascending atomic weights as being more suitable for analytical practice.

A. Reactions of the Cations.

The cations of salts, the reactions of which are described in the following pages, are metals; and with these is included the complex ion ammonium, which behaves in all respects as a metal In the first place a general survey is given of the respective metals (cations) belonging to the different groups.

The elements of more frequent occurrence or of more practical importance are printed in italics, and are dealt with more fully in the following sections. The rarer elements are enclosed in brackets. Their behaviour towards reagents is described somewhat more briefly. These sections may be omitted at first in the study of qualitative analysis.

The classification into groups is based essentially upon the differing solubility of the chlorides in water, of the sulphides in water, acids, and ammonium sulphide, and of the hydroxides, phosphates, or carbonates in water. *For the separation of the groups the following reagents are, therefore, used: Hydrochloric acid, hydrogen sulphide, ammonium sulphide, ammonia, ammonium carbonate,* and *sodium ammonium hydrogen phosphate.*

FIRST GROUP.

None of the group reagents produces a precipitate: (Lithium), *Sodium, Potassium, Ammonium* (Rubidium), (Cæsium).

SECOND GROUP.

Sodium ammonium hydrogen phosphate, and also, in the case of the last three members of the group *Ammonium Carbonate*, produces a precipitate, whereas the other group reagents do not: *Magnesium, Calcium, Strontium, Barium*, (Radium)

THIRD GROUP.

Ammonia, and also *Ammonium Sulphide*, precipitate these metals as hydroxides, whilst *hydrochloric acid* and *hydrogen sulphide* do not produce a precipitate: (Beryllium), *Aluminium*, (Scandium), (Titanium), *Chromium*, (Thorium), (Yttrium), (Zirconium), (Niobium), (Lanthanum), (Cerium), (Prasecodynium), (Neodymium), (Samarium), (Europium), (Gadolinium), (Terbium), (Dysprosium), (Holmium), (Erbium), Ytterbium), (Lutetium), (Tantalum).

FOURTH GROUP.

Ammonium sulphide precipitates the metals as sulphides. *Hydrochloric acid* and *hydrogen sulphide* (in acid solution) cause no precipitations: (Vanadium), *Manganese*, *Ferrous* and *Ferric ion*, *Cobalt, Nickel, Zinc*, (Gallium), (Indium), (Thallium), (Uranium).

FIFTH GROUP.

Hydrogen sulphide precipitates (from acid or alkaline solution) and so does *ammonium sulphide* the metals as sulphides, which are *insoluble in ammonium sulphide*; some of the substances in Group V. are also precipitated by hydrochloric acid (First division); *Silver, Mercurous ion, Lead*; whereas others are not precipitated (Second division); *Copper* (Ruthenium), (Rhodium), (Palladium), *Cadmium*, (Osmium), *Mercuric ion, Bismuth*.

SIXTH GROUP.

Hydrogen sulphide precipitates from acid but not from alkaline solution the metals as sulphides, which are soluble in *ammonium sulphide*: (Germanium), *Arsenite and Arsenate ion*,[1] (Selenium), (Molybdenum), *Stannous and Stannic ion*, *Antimony*, (Tellurium), (Tungsten), (Iridium), *Platinum, Gold*.

The general survey of the arrangement of anions in groups is given at the beginning of the description of the individual ions.

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[1] Although it almost always occurs in its compounds as anion, arsenic is grouped with the cations, because its behaviour towards hydrogen sulphide causes it to separate with the cations, and hence it must be taken into consideration in the systematic investigation of cations.

III. REACTIONS OF THE INDIVIDUAL CATIONS.

FIRST GROUP.

Cations of the Alkali Metals.

SEC. 27.

Members of frequent occurrence: **Potassium, Sodium, (Ammonium).**

Members of less frequent occurrence: **Cæsium, Rubidium, Lithium.**

Characteristics of the Group.

Position of the members in the periodic system.—All the *alkali metals* in the first group of the periodic system, and, with the exception of sodium, occupying the left-hand side (unrelated members), are more strongly electropositive (less noble, see p. 31) in proportion as their atomic weight is greater. With the exception of lithium they are the most strongly positive elements. Hence they have a great tendency to form ions; their compounds are dissociated to a pronounced extent in aqueous solution (ammonium hydroxide in aqueous solution to a much less extent) The hydroxides of the alkali metals are, therefore, strong bases Their aqueous solutions are termed lyes The salts of alkali metals with weak acids (p. 25) therefore show in aqueous solution considerable hydrolysis (ammonium salts to a less extent) (see p. 28) Hence, owing to their containing hydroxyl ions the aqueous solutions of hydroxides, sulphides, and borates of the alkali metals turn red litmus paper blue and turmeric paper brown in a marked degree The solutions of the salts of the alkali metals with strong acids (p. 19) show a neutral reaction.

Analytical Character. The hydroxides, sulphides, and salts of the alkali metals and of ammonium are all, or nearly all, readily soluble in water. Hence, the group reagents, hydrochloric acid, hydrogen sulphide, ammonium sulphide, ammonium carbonate, and phosphate do not produce precipitates in the salts of the alkali metals (in the case of lithium salts this only applies to the more dilute solutions).

SPECIAL REACTIONS OF THE MEMBERS OF GROUP I OF MORE FREQUENT OCCURRENCE.

SEC. 28.

(a) Potassium, K, 39·10.

1. *Potassium* is a monovalent metal of sp. gr. 0·8629 at 0°, melting at 62·5°. It is silvery white and unstable in the air, forming by

oxidation and attraction of water the white *hydroxide*, KOH. This liquefies on exposure to the air, and the resulting oily fluid rapidly absorbs carbon dioxide from the atmosphere, but does not solidify in the process. Potassium decomposes water into hydrogen (which escapes in gaseous form and ignites on contact with the incandescent metal) and hydroxyl ions, while, on its part, it forms potassium ions. Potassium burns in the air, forming a mixture (dark while hot and orange-yellow on cooling) of *potassium oxide*, K_2O, and *potassium peroxide*, K_2O_2, which attracts moisture from the air, and decomposes into potassium hydroxide, oxygen, and hydrogen peroxide. Nearly all the potassium salts are soluble in water; they are colourless, excepting when the anion causes them to be coloured.

2. **At a low ignition temperature** (when heated in a small bulb tube over a gas flame) the *oxides, hydroxide*, and the *salts of potassium are not volatile (distinction from ammonium compounds).*

3. **Platino-hydrochloric acid** (platinum chloride solution) *produces in neutral and acid solutions of potassium salts a heavy yellow crystalline precipitate of potassium platino-chloride*, K_2PtCl_6, *immediately in the case of concentrated solutions, but only after a considerable or long time when the solutions are more dilute No precipitates are produced in very dilute solutions*

$$2K^{\cdot} + PtCl_6'' = K_2PtCl_6, \text{ e g } 2KCl + H_2PtCl_6 = K_2PtCl_6 + 2HCl$$

The precipitate consists of octahedra, which can be recognised under the microscope. *Alkaline* solutions must be acidified with hydrochloric acid prior to the addition of the platino-hydrochloric acid. The precipitate is sparingly soluble in water; its solubility is not appreciably increased by the presence of free acids It is insoluble in *alcohol*. Hence platino-hydrochloric acid gives a particularly sharp test for potassium ions, if the reaction is made to take place in presence of alcohol. The reaction is most sensitive when the aqueous solution of the potassium salt is evaporated with platino-hydrochloric acid nearly to dryness on the water-bath, and the residue then treated with a little water (or better still alcohol, if no substances insoluble therein are present), which will leave the potassium platino-chloride undissolved. The precipitate must not be mistaken for ammonium platino-chloride (Sec. 30, 5). *Large quantities* of sodium salts affect the sensitiveness of the reaction.

4. **Tartaric acid solution,**[1] $[CH(OH)COO]_2H_2$, *produces in a*

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[1] Tartaric acid solutions become mouldy on standing, and should, therefore, be freshly prepared each time.

neutral or alkaline[1] *solution of potassium salts a white granular crystalline precipitate of potassium hydrogen tartrate*, $[CH(OH)COO]_2HK$ (or $KHC_4H_4O_6$), *which rapidly subsides.* The precipitation takes place immediately in concentrated solutions, but often only after a considerable time in dilute solutions. No precipitate is obtained with very dilute solutions Vigorous shaking or stirring of the liquid materially promotes the formation of the precipitate. It is dissolved by alkalis and mineral acids; it is sparingly soluble in cold water, but fairly soluble in hot water. In testing acid solutions for potassium ions with tartaric acid, the free acid must first be removed by evaporation or ignition, or neutralised by the addition of sodium hydroxide or carbonate.

Better results are obtained by the use of **sodium hydrogen tartrate,** $NaHC_4H_4O_6$, *instead of free tartaric acid.* The reaction shows the same phenomena, but is more sensitive, because no hydrogen ions are formed, *i.e.* no free acid is produced in which the precipitate dissolves more readily than in water:

$$K^{\cdot} + [H^{\cdot} + HC_4H_4O'_6] = KHC_4H_4O_6 + H^{\cdot}$$

but

$$K^{\cdot} + [Na^{\cdot} + HC_4H_4O'_6] = KHC_4H_4O_6 + Na^{\cdot}$$

as, for example

$$KCl + H_2C_4H_4O_6 = KHC_4H_4O_6 + HCl$$

but

$$KCl + NaHC_4H_4O_6 = KHC_4H_4O_6 + NaCl$$

The reaction is also more sensitive from the fact that sodium hydrogen tartrate is more strongly dissociated than tartaric acid, so that the same quantity of hydrogen tartrate ion is present in a smaller amount of liquid.

5. *Perchloric acid: An aqueous solution of perchloric acid*, $HClO_4$, *produces in neutral, acid, or alkaline solutions a white crystalline precipitate of potassium perchlorate*, $KClO_4$. This is sparingly soluble in cold water, and practically insoluble in alcohol. It is only slightly soluble in acids or alkali hydroxide solution. Ammonium salts do not give a precipitate with perchloric acid

6. A freshly prepared mixture of *sodium nitrite solution* (2 c.c. of a 10 per cent. solution), *cobalt nitrate solution* (five or six drops) and *acetic acid* (1 c.c.) produces in a neutral solution of potassium salts a yellow crystalline precipitate of *potassium cobaltinitrite*, $K_3[Co(NO_2)_6]$,[2] or of double salt of sodium and potassium, $NaK_2[Co(NO_2)_6]$ or $Na_2K[Co(NO_2)_6]$. In concentrated solutions the

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[1] In the case of alkaline solutions the reagent should be added until the reaction is strongly acid.

[2] For particulars of the properties of the precipitate, see *Cobalt*, Sec 60, 15.

precipitate appears immediately, but only after some time in dilute solutions. It is also obtained even in the presence of large quantities of sodium salts. When the latter are present this reaction is to be preferred to that with platino-hydrochloric acid.

Before applying the test, alkaline solutions should be rendered just acid with acetic acid, and acid solutions freed from acid by evaporation, or when this is not practicable, they should be neutralised with sodium carbonate. Ammonium salts give a similar reaction, but only in concentrated solution. When it is a question of detecting small amounts of potassium, L. T. Bowser (*Chem. Zentralbl.*, 1910, II., 755; and 1911, II., 1838) recommends the addition of an equal volume of alcohol, which should cause an immediate precipitation. Ammonium salts must first be removed.

According to Burgess and Kamm (*Chem. Zentralbl.*, 1912, II., 808), the addition of a small amount of silver nitrate increases the sensitiveness of the reaction. The precipitate consists of $AgK_2CO(NO_2)_6$ or $Ag_2KCo(NO_2)_6$. Obviously the reaction can only be used in solutions free from chlorides. Other metals, except sodium, must not be present, since other double compounds of silver with cobaltinitrite are also only sparingly soluble.

7. *An alcoholic solution of sodium bismuth thiosulphate* gives, even with minute quantities of potassium salts a yellow precipitate of *potassium bismuth thiosulphate.*[1] The presence of the chlorides of ammonium,[2] sodium, calcium, or magnesium does not interfere with the reaction.

For the preparation of the reagent (which cannot be kept without decomposition) 7 7 grms. of sodium thiosulphate are dissolved in 50 c.c. of water, and 5 grms. of bismuth nitrate with the *smallest possible quantity* of hydrochloric acid also in 50 c.c. of water. Equal volumes of the two solutions are mixed (1 to 2 drops of each), 10 to 15 c.c. of absolute alcohol added, and then sufficient water to give a clear solution. To this is added drop by drop the liquid to be tested for potassium (Carnot, *Ber.*, **9**, 1131; Campari, *Zeitsch. anal. Chem.*, **23**, 6; Pauly, *ibid.*, **36**, 512).

8. *Silicohydrofluoric acid*, H_2SiF_6, added in excess to a solution of a potassium salt produces an almost transparent gelatinous precipitate of *potassium silicofluoride*, K_2SiF_6. The solution must

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[1] The sensitiveness of the reaction depends mainly upon the proportions of alcohol and water in the liquid. Pauly was able to detect 0·00005 grm. of CKl with certainty.

[2] We are unable to confirm the statement that ammonium chloride prevents the occurrence of the reaction.

not be alkaline or the silicofluoride ion will be decomposed, with the separation of silicic acid: $4OH' + SiF''_6 = Si(OH)_4 + 6F'$. This precipitate might be mistaken for potassium ion.

9. The usual reagents for alkaloids, *picric acid* (or sodium picrate), *sodium phosphotungstate*, and *phosphomolybdic acid* (on heating with the solution and subsequent cooling) all produce precipitates in solutions of potassium salts, that produced by picric acid being yellow and that by phosphotungstic acid white and crystalline. The precipitate produced by phosphomolybdic acid is formed, especially when only a small amount of potassium salt is present, as a yellow deposit on the sides of the vessel.

10. **Dipotassium hydrogen pyro-antimonate** (Sec. 29, 3) *produces no precipitate in neutral or alkaline solutions of potassium salts.* (Distinction from sodium.)

11. **At a strong ignition heat** potassium salts volatilise, and the more readily in proportion to the volatility of their anions (*cf.* p. 91). *Hence they volatilise in a gas or spirit flame*, to which they impart a bluish-violet coloration.

In order to produce the reaction a small quantity of the solid substance is introduced on a loop of platinum wire into the fusion area of a gas flame[1] (Fig. 26, p. 81), or its solution is blown into the flame from a spraying apparatus (Figs. 37 and 38, p. 98). Spirit flame colorations may also be produced by heating a potassium salt (preferably potassium chloride) with a little water, adding spirit which burns with a colourless flame, and igniting the mixture. The presence of a sodium salt completely masks the potassium coloration. The use of light filters (cobalt glass or indigo or permanganate prisms, Sec. 22),[2] will eliminate the disturbing influence of sodium, calcium, and lithium compounds. Any organic substances present, which would make the flame luminous, must be removed by a preliminary ignition. The use of the spectroscope is much more certain (Sec. 22).

The spectrum of the potassium flame is represented in Table I. It contains two characteristic lines, the red α (769·9$\mu\mu$) and the indigo-blue β (404·4$\mu\mu$).

12. For details of the *microchemical detection* of potassium, see Haushofer, *Mikroskopische Reaktionen*, p. 55; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 26; Schoorl, *Zeitsch. anal. Chem.*, **48**, 601, 609; Frey, *ibid.*, **32**, 204; Huysse, *ibid.*, **39**, 9; Borkorny, *Chem. Zentralbl.*, 1913, I., 640.

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[1] Decrepitating salts are previously fused in a platinum spoon.

[2] Other light filters are recommended by Alois Herzog, *Chem. Zeit.*, **42**, 145; *Zeitsch. anal. Chem.*, **57**, 373.

SEC. 29.

(b) **Sodium,** Na, 23·00.

1. Sodium is a monovalent metal of sp. gr. 0·972 at 0°, and with a melting point of 97·6°. Its colour is silvery white. It is unstable in (moist) air, and behaves in an analogous manner to that of potassium in forming white *sodium hydroxide*, NaOH. It decomposes water without igniting the liberated hydrogen. Sodium hydroxide liquefies on exposure to air to an oily fluid, which soon becomes solid again through the absorption of carbon dioxide and formation of carbonate. Crystallised sodium carbonate, $Na_2CO_3+10H_2O$, rapidly effloresces when exposed to the air, as does also the sulphate $Na_2SO_4+10H_2O$. Sodium chloride dissolves more readily in water than in concentrated hydrochloric acid, since the solubility product $[Na^{\cdot}] . [Cl']$ is obviously formed, even in the case of lower $Na^{\cdot}$ concentrations, by the excess of Cl' ions (p. 33). Speaking generally, the sodium salts behave essentially in the same manner as potassium salts.

When sodium burns in the air *sodium oxides* are produced, notably the white *peroxide*, Na_2O_2.

2. Sodium compounds do *not* volatilise at **a low ignition temperature.**

3. **A saturated solution** of **dipotassium dihydrogen pyro-antimonate**[1] *produces in sufficiently concentrated neutral* or *alkaline solutions* of sodium salts a *white crystalline precipitate* of disodium dihydrogen pyro-antimonate, $Na_2H_2Sb_2O_7+6H_2O$. This reaction is best carried out in a clock-glass. The precipitate (owing to its being invariably crystalline) does not form immediately, and at first only a slight turbidity is usually produced, but on rubbing the glass below the liquid with a glass rod the precipitate rapidly separates, and is deposited first of all upon the rubbed places in the form of a heavy sand-like powder.

The salt only separates after a long time (*e.g.* in 12 hours) from dilute solutions of sodium salts, and not at all from very dilute solutions. The separated sodium pyro-antimonate is *invariably crystalline*. When slowly deposited it sometimes consists of well-formed microscopic tetragonal pyramids resembling octahedra, but more often of tetragonal pyramidal pointed prisms; when rapidly precipitated it has the form of small boat-shaped crystals. The presence of a large quantity of potassium salts has a very considerable influence on the reaction. *Acid solutions* cannot be tested with dipotassium dihydrogen pyro-antimonate, since free acids liberate *pyro-antimonic acid*, ($H_4Sb_2O_7$), from the latter. Hence, whenever possible, free acid must be removed by evaporation or ignition, or, if this is not practicable, by adding sufficient potassium carbonate to produce a faintly alkaline reaction before adding the reagent. In neutral solutions the presence of ammonium salts of strong acids also causes a separaton of pyro-antimonic acid after a short period of standing. This is due to the fact that ammonium salts undergo hydrolytic dissociation, and that their solution through evaporation acquires an acid reaction. A further precaution is that only solutions which contain no other cations than those of sodium and potassium and, under certain conditions, of ammonium, must be tested with dipotassium dihydrogen pyro-antimonate.

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[1] With regard to its preparation, see p. 112.

4. **Platino-hydrochloric acid, tartaric acid** (or sodium hydrogen tartrate), **perchloric acid,** *sodium bismuth thiosulphate*, *sodium picrate*,[1] *phosphotungstic acid*, and *sodium phosphomolybdate* give no precipitates with sodium salts in aqueous solution.

5. A mixture of *bismuth nitrate* and *potassium nitrite* (slightly acidified with nitric acid), to which a little *cæsium nitrate* has been added, produces in solutions of sodium salts a yellow crystalline precipitate with the composition $5Bi(NO_2)_3\ 9CsNO_2\ 6NaNO_2$. It is a very sensitive reaction, and only *a little* of the solution under examination need be used Heavy metals interfere with the test. W. Craven Ball, *Chem Zentralbl.*, 1910, I., 1, 765 (*cf* also Sec 32, p 134).

6. When *sodium salts* are introduced into the **fusion area of the flame** of a *Bunsen burner* or spirit lamp *volatilisation* takes place, as in the case of potassium salts Sodium salts are somewhat less volatile than the corresponding potassium salts The *intense yellow flame coloration* which appears when sodium salts are volatilised is *extremely characteristic* ; it enables the smallest quantity of a sodium compound to be detected, and is not affected by considerable quantities of potassium salts.

The **spectrum of the sodium flame** (Table 1) shows when examined with an ordinary spectroscope, only *one* yellow line α. But by the use of apparatus with greater dispersion it is recognised that the yellow stripe consists of two distinct lines ($589{\cdot}6\mu\mu$ and $589{\cdot}0\mu\mu$) quite close to each other. The reaction is so extraordinarily sensitive that, as a rule, the ordinary salt in the atmospheric dust is sufficient to produce a sodium spectrum, if only a faint one.

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[1] Sodium carbonate is precipitated by sodium picrate.

7. With regard to the *microchemical detection* of sodium, see Haushofer, *Mikroskopische Reaktionen*, p. 98; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 31; Schoorl, *Zeitsch. anal. Chem.*, **48**, 604; Lenz and Schoorl, *ibid.*, **50**, 263; Frey, *ibid.*, **32**, 204.

SEC. 30.

(c) Ammonium, NH_4.

1. Ammonia, NH_3, at the ordinary temperature, is a colourless gas with a penetrating odour. At a lower temperature and under high pressure it is condensed to a colourless, mobile liquid, with a strongly refractive action on light.

Ammonia gas dissolves very readily in water. This solution shows an *alkaline* reaction towards litmus, turmeric, and other indicators, and thus contains hydroxyl ions and, as cation, the ammonium ion $NH_4^{\cdot}$. When dissolved in water there is an immediate addition of one molecule of water, whereby the nitrogen atom is transformed from the trivalent into the pentavalent condition: $NH_3+H_2O = NH_4OH$ (or $NH_4^{\cdot}+OH'$). The solution contains, however, considerably less free hydroxyl ions (is faintly alkaline) than corresponds to the amount of ammonia gas in solution. This may be due either to the fact that *ammonium hydroxide* is only slightly dissociated, or that a part of the ammonia is simply dissolved unaltered, without combining chemically with the water. Ammonia combines with acids by addition to form ammonium salts, *e.g.* $NH_3+HCl = NH_4Cl$ (or $NH_4^{\cdot}+Cl'$).

The monovalent group *ammonium*, NH_4, behaves in every respect in an analogous manner to that of a metal, which must closely resemble potassium. Ammonium is unknown in the uncombined condition, but an alloy with mercury, an ammonium amalgam can be prepared.

2. *Ammonium salts are all volatile* **at a low ignition temperature,** and subside again on cooling in the form of *sublimates* (p. 55). During the volatilisation there is always a partial decomposition of the salt into ammonia and free acid (p. 13). If the latter only volatilises with difficulty, as *e.g.* phosphoric acid, practically only the ammonia escapes. *In this case little, if any, sublimate is formed.*

3. *Ammonium salts are nearly all readily soluble in water.* The solutions are colourless, except when the anion causes them to be coloured. Ammonium salts are strongly dissociated in aqueous solution, and hence the solutions of the salts with strong acids show

a neutral reaction (p. 25). The salts of weak acids, *e.g.* ammonium carbonate, undergo partial hydrolytic dissociation (p. 28); they have an alkaline reaction and smell of ammonia.

On boiling aqueous solutions, and even on evaporating them, a partial hydrolytic dissociation into ammonia and acid occurs, even in the case of the ammonium salts of strong acids. The ammonia evaporates to a greater extent than the acid, so that the reaction becomes acid.

4. *When ammonium salts are triturated with* **slaked lime (calcium hydroxide),** preferably with the addition of a few drops of water, or when they are heated in solid form or solution with **potassium hydroxide** or **sodium hydroxide solution,** *the ammonia is liberated in gaseous form,* and may be identified firstly by its *odour*, secondly by its *reaction* on moistened test paper, and thirdly by the fact that it produces *white fumes* when brought into contact with an object (a glass rod) moistened with hydrochloric, nitric, or acetic acid, or in fact with any *volatile acid.* These fumes are due to the formation of solid salts when the gases meet in the air. Hydrochloric acid gives the most sensitive reaction, but acetic acid is less liable to lead to a mistake

If the ammonia is expelled in a small beaker, preferably by means of calcium hydroxide in presence of a very little water, and the beaker is covered with a clock-glass to the centre of the convex side of which a piece of moistened turmeric paper or litmus paper is attached, it is possible to detect even minute quantities of ammonium; but in this case the reaction does not take place at once, but only after some time. It is accelerated by gentle heating. Care must be taken that the moist reagent paper does not come into contact with particles of calcium hydroxide (*cf* also 12)

5. **Platino-hydrochloric acid** behaves towards ammonium salts in the same way as towards potassium salts. The resulting yellow precipitate of *ammonium platinochloride*, $(NH_4)_2PtCl_6$, is composed, like the corresponding potassium compound, of octahedra, as can be seen under the microscope.

6. **Tartaric acid solution** precipitates, after some time from very concentrated neutral solutions of ammonium salts, a portion of the ammonium as *ammonium hydrogen tartrate*, $(NH_4)HC_4H_4O_6$, but solutions which are at all dilute do *not* yield a precipitate. **Sodium hydrogen tartrate solution** effects a more complete precipitation from concentrated solutions, and even produces a precipitate in more dilute solutions. Ammonium hydrogen tartrate is a white crystalline

precipitate ; shaking and rubbing the sides of the glass vessel promote its separation. It behaves towards solvents in the same way as the corresponding potassium salt, excepting that it is somewhat more soluble in water and acids.

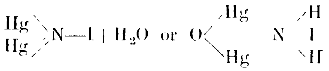
7. *Picric acid*, *sodium tungstate*, and *phosphomolybdic acid* have an analogous action upon ammonium salts and potassium salts. The *cobaltonitrite reagent* (*cf.* Sec 28, 6) gives with concentrated solutions of ammonium salts a precipitate similar to that obtained with potassium salts

8. **Perchloric acid** gives *no* precipitate with solutions of ammonium salts. (Distinction from potassium.)

9. **Dipotassium dihydrogen pyro-antimonate** does *not* produce a crystalline precipitate with ammonium salts. (Distinction from sodium ; see, however, p. 125.)

Mercurous and mercuric salts when added to solutions containing ammonium ions produce various complex compounds, some of which are of importance for the detection of small quantities of the ammonium ion. All these compounds may be regarded as ammonium salts (containing, therefore, the N in pentavalent condition), in which the hydrogen atom is wholly or partially replaced by mercury, or as double salts of mercury, in which, in addition to another anion, the monovalent radicle amide NH_2 (containing the N in a trivalent condition) is present. In the explanation of the following reactions, numbered 10 to 12, we have adopted the former hypothesis.

10. *Nessler's reagent*[1] (an alkaline solution of mercuric potassium iodide) produces in a liquid containing ammonia or an ammonium salt a red-brown precipitate (or in *very* dilute solution only a yellow coloration, which at the extreme limit of dilution may only appear after a considerable time). This precipitate consists of dimercuric ammonium iodide, $NHg_2I + H_2O$



The reaction takes place in accordance with the equation

$$2HgK_2I_4 + 3KOH + NH_4OH = (NHg_2I + H_2O) + 7KI + 3H_2O.$$

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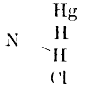
[1] This is prepared by dissolving 35 grms. of potassium iodide and 13 grms. of mercuric chloride in 8700 c.c. of water, the liquid being heated to boiling and stirred until a clear solution obtained. To this is added, drop by drop, a cold saturated solution of mercuric chloride until a permanent precipitate begins to be formed. At this stage 160 grms. of potassium hydroxide or 120 grms. of sodium hydroxide are added, and the liquid diluted with water to 1 litre, and after the addition of a little more mercuric chloride solution, allowed to settle. The clear solution has only a slight yellowish colour.

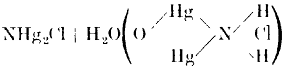
Warming the liquid promotes the separation of the precipitate. Cyaides, sulphides, and hydrocarbonates of the alkali metals, as also free carbon ioxide, interfere with the reaction. It is also prevented by the presence f soluble salts of alkali metals, and, in general, of such substances as form recipitates with alkali hydroxides.

Nessler's reagent is especially used in testing natural waters for ammoaum. For particulars reference may be made to Part II, Chapter II., lec. 168.

11. A few drops of a solution of *mercuric chloride* produce in aqueous olutions of ammonia or ammonium carbonate, even when very dilute, a hite precipitate of mercuric ammonium chloride, NH_2HgCl:



In the case of exceedingly dilute solutions no turbidity is produced, but n adding a few drops of potassium or sodium carbonate solution a white urbidity or opalescence is obtained after a few minutes, even when the lilution has been carried to an extreme limit. This reaction occurs when water which contains a trace of a neutral ammonium salt is treated with a ew drops of a solution of mercuric chloride and a few drops of a solution f potassium or sodium carbonate. The precipitate which separates on he addition of alkali carbonate has the composition



are must be taken when adding the mercuric chloride and alkali carbonate hat the amounts of these are not sufficient to cause a yellow precipitate of nercuric oxide to be formed (Bohlig, Schoyen [1]). The reaction has also een recommended for the examination of natural waters. Ferraro [2] calls ttention to the fact that in this case, under certain conditions, water free from ammonium ion may also yield white precipitates of mercuric hydroxide r oxychloride, or of a double carbonate of mercury and calcium, but that these may be distinguished from mercuric ammonium chloride by being onsiderably more soluble in acetic acid. The reaction, unlike that btained with Nessler's reagent, also takes place in alcoholic solutions (De Koninck [3]).

12. On adding a solution of *mercurous nitrate* to a liquid containing free ammonia or ammonium carbonate, a black (or in the case of very dilute solutions a greyish-white) precipitate is obtained. This is a mixture of the precipitate produced by mercuric compounds (see 11) with metallic mercury (see Sec. 71, 6).

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[1] *Zeitsch. anal. Chem.*, **2**, 330.
[2] *Boll. Chim. Farm.*, **39**, 797; *Chem. Zentralbl.*, 1901, I., 203.
[3] *Chem. News*, **69**, 220; *Chem. Zentralbl.*, 1894, I., 1096.

Hence, if the ammonia liberated according to (4) is brought into contact with a glass rod moistened with mercurous nitrate and introduced into the test-tube, or with a drop of the solution suspended from the convex side of a clock-glass covering the beaker in which the ammonia is being developed, or with a strip of paper moistened with the reagent and placed beneath the clock-glass, the drop or the paper strip will become grey or black. This method of applying the test may be recommended, because the presence of large quantities of salts may influence or prevent the reaction.

13. If a few drops of a 10 per cent. solution of *potassium iodide* and a drop of a saturated solution of *sodium hypochlorite* (*Eau de Javelle*) are added to a solution containing ammonia or an ammonium salt, a black precipitate of nitrogen iodide is obtained

$$2NH_4Cl + 2KI + 2ClONa = NHI_2 + NH_3 + 2KCl + 2NaCl + 2H_2O$$

or

$$2NH^{\cdot}_4 + 2I' + 2ClO' = NHI_2 + NH_3 + 2Cl' + 2H_2O$$

The reaction is very sensitive (Trillat and Turchet [1])

14. On adding 10 to 15 drops of a solution of paranitro-azobenzene [2] to 10 c.c. of the solution to be tested for ammonia or an ammonium salt, shaking the tube vigorously, and slowly adding, drop by drop, 10 per cent. sodium hydroxide solution, a reddish-yellow cloud is obtained, which, on further shaking, imparts a yellow to red colour to the solution. The addition of sulphuric acid in excess decolorises the solution and causes the separation of microscopic yellow needles. The reaction is very sensitive, and is obtained with all substances which yield ammonia under the action of alkalis (Riegler [3]). The reaction is based upon the formation of the coloured ammonium salt of *p*-nitrophenylnitrosamine.

For further reactions for the detection of small quantities of ammonia, especially in the air, see *Zeitsch. anal. Chem.*, **21**, 560; **39**, 577; *Chem. Zentralbl.*, 1912, II., 1397.

15. For the microchemical detection of the ammonium ion, reference may be made to Haushofer, *Mikroskopische Reaktionen*, p. 13; and Behrens-Kley, *Mikrochem. Analyse*, 3rd ed., p. 36.

SEC. 31.

Summary and Remarks on Group I.

1. The detection of potassium ions is only possible by means of most reagents when ammonium ions are not also present. The

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[1] *Comptes rend.*, **140**, 371; *Chem. Zentralbl.*, 1905, I., 832.

[2] The reagent is prepared by heating 1 grm. of paranitroaniline with 20 c.c. of water and 1 c.c. of hydrochloric acid, diluting the resulting solution (with vigorous shaking) with 160 c.c. of water, and, after cooling, adding 20 c.c. of a 2·5 per cent. solution of sodium nitrite, and shaking the flask until everything has dissolved. The reagent becomes turbid after some time, but may be rendered fit for use again by filtration.

[3] *Chem. Zeit.*, **21**, Rep. 307.

presence of ammonium salts also interferes with the detection of the sodium ion by means of dipotassium dihydrogen pyro-antimonate.

Hence, before testing for potassium or sodium, any ammonium salts present must be removed by *gentle* ignition, until visible vapours no longer escape. (The detection of ammonium salts may be readily effected, even in the presence of potassium and sodium salts, by liberating the ammonia by means of calcium hydroxide.) The *residue from the ignition* is dissolved in the *smallest possible* quantity of water. Owing to the relatively great solubility of the salts which serve for the detection of the alkali metals, all reactions for alkali ions are only obtained with certainty in concentrated solutions. A decision may thus be reached with one drop of a concentrated solution, whilst the result may often be uncertain with a large amount of a dilute solution. The detection of *sodium* is effected by means of dipotassium dihydrogen pyro-antimonate, close attention being paid to the conditions of the reaction, and the nature of the precipitate (*cf.* Sec. 29, 3). The *potassium ion* is detected by means of platino-hydrochloric acid, or sodium hydrogen tartrate, or, better, in presence of a large excess of sodium ion, by means of the cobaltonitrite reagent. If the potassium ion is to be detected *in the presence of* ammonium ion perchloric acid is used.

2 Potassium is most easily identified in potassium platino-chloride, perchlorate, and hydrogen tartrate after a preliminary decomposition of these salts by gentle ignition. The platinum compound (the decomposition of which is facilitated by the addition of a little oxalic acid) and the perchlorate yield potassium chloride, whilst potassium hydrogen tartrate yields sodium carbonate. Potassium cobaltinitrite yields, on ignition with sulphuric acid, potassium sulphate and cobaltous sulphate For the direct detection of potassium in potassium iodide, tartaric acid or sodium hydrogen tartrate are more suitable than platino-hydrochloric acid or the cobaltonitrite reagent, since the addition of the former produces a deep red coloration, due to platinic iodide and free iodine, which to some extent conceals the separation of the potassium platino-chloride, whilst nitrites decompose iodides in the presence of acids, with the separation of iodine

3. When small quantities of sodium ion are to be detected in the presence of a large amount of potassium ion, the latter is first separated by means of platino-hydrochloric acid, the platinum removed from the filtrate by means of hydrogen sulphide, the filtrate from this precipitate evaporated to dryness, the residue gently

ignited and dissolved in a little water, and the solution tested with dipotassium dihydrogen pyro-antimonate.

4. The potassium and sodium ions may be readily detected with very much more speed by means of the flame colorations than by the wet method, and the test is infinitely more sensitive. The sodium coloration, however, completely masks the potassium coloration, even when only a small quantity of sodium is present; but when a spectroscope is used, the spectra of both metals appear so sharply and clearly that a mistake is impossible. The presence of sodium chloride intensifies the strength of the potassium lines up to a proportion of 100 of sodium chloride to 1 of potassium chloride; but in presence of a larger proportion of sodium chloride the sensitiveness of the spectroscopic detection decreases again (Gooch and Hart).

If a spectroscope is not available the colour of the potassium flame may be easily recognised, even in an intense yellow sodium flame, by the aid of a glass prism filled with a solution of indigo or potassium permanganate, by means of the light filters recommended by Herzog (see p. 123, footnote 2), or by means of blue glass.

SEC. 32.

SPECIAL REACTIONS OF MEMBERS OF THE FIRST GROUP OF LESS FREQUENT OCCURRENCE.

1. **Cæsium,** Cs, 132·81, and 2. **Rubidium,** Rb, 85·45.

The compounds of cæsium and rubidium, especially those of the latter, are widely distributed in nature, but only in very small quantities. They have been found in the mother liquors of many mineral waters, and in a few minerals (lepidolite, carnallite), cæsium in greater quantity in pollux, and rubidium in beetroot molasses and plant ashes.

Cæsium and *rubidium* are silvery-white metals closely resembling potassium in all their characteristics. The melting point of cæsium is 26·4°, that of rubidium 38·5°; the sp. gr. of cæsium is 1·88, that of rubidium 1·52. Speaking generally, the compounds of cæsium and rubidium are very similar to those of potassium. Thus, they are precipitated from their aqueous solutions by *platino-hydrochloric acid*, and their volatile compounds also impart a violet coloration to a non-luminous flame on ignition. With regard to the solubility of the salts of potassium, rubidium, and cæsium, it may be stated that as a general rule the solubility of the simple salts increases with the rise in atomic weight from potassium to cæsium, whilst in the case of the complex salts it decreases from potassium to cæsium. Hence the precipitates given by cæsium and rubidium with platino-hydrochloric acid are far more insoluble in water than potassium platinochloride. For example, 100 grms. of water at 10° will dissolve

900 mgrms. of potassium platinochloride, but only 154 mgrms. of rubidium platinochloride, or 50 mgrms. of cæsium platinochloride. The alums also show great differences in their solubility in cold water. Thus, 100 parts of water at 17° dissolve 13·6 parts of potassium alum, 2·27 parts of rubidium alum, and 0·619 part of cæsium alum.

The metals are most readily distinguished from each other and from potassium by the fact that flames coloured by cæsium and rubidium compounds yield *spectra* quite different from the potassium spectrum (Table I.). In the cæsium spectrum the two blue lines *α* 455·5*μμ* and *β* 459·3*μμ*, which are extraordinarily sharp and distinct, are particularly characteristic, whilst adjoining them is also to be noted the less prominent line *γ* 601·6*μμ*. In the rubidium spectrum the beautiful indigo blue lines *α* 420·2*μμ* and *β* 421·6*μμ* of extraordinary intensity first catch the eye; less intense, but still more characteristic, are the red lines *γ* 620·7*μμ* and *δ* 629·9*μμ*. When both alkali metals are to be spectroscopically identified in the presence of each other, the chlorides, not the carbonates, should be chosen, since in the case of the latter the rubidium spectrum does not always appear distinctly in association with the cæsium spectrum (Allen, Heintz). Lastly, it should be mentioned that cæsium carbonate is soluble, whilst rubidium carbonate is insoluble in absolute alcohol. It is difficult, however, to effect a separation in this way, since the two metals appear to form a double salt which is not entirely insoluble in alcohol. A better method of separation is by means of the hydrogen tartrates, that of rubidium being soluble in 8·5 parts of boiling water and in 84·57 parts at 25°; whilst cæsium hydrogen tartrate dissolves in 1·02 part of boiling water and in 10·32 parts at 25° (Allen), and potassium hydrogen tartrate requires for solution 16 parts of boiling water and 77 parts at 25°. The most trustworthy process of separating potassium and rubidium from cæsium is based upon the above-mentioned insolubility of the complex salts of cæsium and heavy metals, and the two following methods depend upon this property.

a. The concentrated solution of the salt is treated with a solution of antimony trichloride in strong hydrochloric acid, and the precipitate of cæsium chloride antimony chloride, $3CsCl,2SbCl_3$, which separates immediately, is collected on a toughened filter and washed with strong hydrochloric acid. All other alkali metals, including ammonium, are not precipitated, but are found together with antimony trichloride in the filtrate (Godeffroy [1]).

b. The hot concentrated solution of the salts containing a considerable amount of strong hydrochloric acid is treated with stannic chloride, and the precipitate of cæsium chlorostannate, Cs_2SnCl_6, collected on a toughened filter, washed with strong hydrochloric acid, and dissolved in boiling water containing a little hydrochloric acid. It is again precipitated with concentrated hydrochloric acid, separated, and again washed with strong hydrochloric acid. The filtrate will contain the rubidium and any potassium present, together with the excess of stannic chloride. Any ammonium that may be present, however, will be found as ammonium stannic chloride in the precipitate. Hence, ammonium salts must be removed beforehand (F. Stolba).[1]

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[1] *Ber.*, 7, 375.

For differentiating between cæsium and rubidium on the one hand, and potassium on the other hand, use may be made of W. C. Ball's observation,[2] that a complex nitrate of bismuth, sodium, and one of the two metals is formed when a little of the solution is added to a very large excess of a solution of 10 grms. of bismuth nitrate and 50 grms. of sodium nitrite in 100 c c. of water acidified with a few drops of nitric acid. In the presence of cæsium or of rubidium a yellow crystalline precipitate is produced (*cf.* Sec. 29, 5).

$$5Bi(NO_2)_3.9CsNO_2.6NaNO_2, \quad \text{or} \quad Bi(No_2)_3.2RbNO_2.NaNO_2$$

For the microscopical detection of cæsium and rubidium, reference may be made to Haushofer, *Mikroskopische Reaktionen*, p. 31 ; Behrens-Kley, *Mikrochem. Analyse*, 3rd ed., pp. 37 and 38 ; E. Denigès, *Chem. Zentralbl.*, 1917, II., 648.

3. **Lithium,** Li, 6·94.

1. *Lithium* is widely distributed in nature, but not in large quantities. It is frequently met with in the analysis of mineral waters, saline mother liquors, and plant ash, but not often in the analysis of technical and pharmaceutical products. In accordance with the general tendency of the elements in the first horizontal series of the periodic system to approximate in their characteristics to the elements occupying the *following* vertical position, lithium forms the transition element between the first and second analytical groups.

Lithium is a silvery-white elastic metal of sp. gr. 0 534, and melts at 180°. It decomposes water, and becomes oxidised in moist air. *Lithium oxide*, Li_2O, dissolves with difficulty in water, and does not become moist on exposure to air.

2. Most *lithium salts* are soluble in water, some (lithium chloride) deliquescent.

3. *Lithium carbonate* dissolves with difficulty. Its solubility increases as the temperature rises. In water containing carbon dioxide it is readily soluble as hydrocarbonate, even in the case of solutions which contain the chlorides of the other alkali metals or of ammonium. The precipitability of the lithium ion by means of ammonium carbonate is, therefore, not important for the *detection* of lithium, but must be noted, since lithium

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[1] *Zeitsch. anal. Chem.*, **12**, 440. Godeffroy (*loc. cit.*) points out that rubidium ion also yields with stannic hydrochloric acid a chlorostannate, which dissolves with difficulty in hydrochloric acid. Cossa also obtained unfavourable results by Stolba's method, and recommends Godeffroy's process. *Zeitsch. anal. Chem.* **17**, 350.

[2] *Chem. Zentralbl.*, 1910, I., 765.

may be partially precipitated together with the carbonates of the second group.

4. *Disodium hydrogen phosphate* produces in not too dilute solutions of lithium salts, at the boiling temperature, a white crystalline precipitate of *normal lithium phosphate*, $2Li_3PO_4 + H_2O$, which rapidly subsides. This characteristic reaction for lithium is rendered far more sensitive by adding to the solution containing the lithium salt disodium hydrogen phosphate and sufficient sodium hydroxide to render it alkaline, and evaporating it to dryness, moistening the residue with water and adding an equal volume of ammonium solution, under which conditions even a very small amount of lithium separates as $2Li_3PO_4 + H_2O$. The precipitate melts over the blowpipe flame, yields transparent beads when fused with sodium carbonate, is absorbed by charcoal, dissolves in hydrochloric acid to a liquid which, when diluted and treated with excess of ammonia, remains clear in the cold, but on boiling yields a heavy crystalline precipitate of the above-mentioned compound. (Distinction from phosphates of the alkaline earth metals.)

5. On treating a not too dilute solution of a lithium salt with *ammonium fluoride* (free from ammonium silicofluoride) and excess of ammonia *lithium fluoride* gradually separates as a white gelatinous precipitate. Since the fluorides of potassium, caesium, and rubidium are readily soluble in water, even when containing ammonia, and sodium fluoride requires only 70 parts of a mixture of equal parts of water and ammonium hydroxide for solution, whereas lithium fluoride requires 3500 parts, it is possible to separate the lithium ion as lithium fluoride, providing that the amount of sodium ion present is not too great. Very small quantities of the lithium ion are best separated by evaporating the solution of the alkali salts, after treatment with ammonium chloride, in a platinum basin on the water-bath, and treating the residue with dilute ammonia solution (A. Carnot [1]).

6. *Tartaric acid* and *platino-hydrochloric acid* do not precipitate lithium salts even from concentrated solutions.

7. When lithium salts are introduced on platinum wire into the non-luminous *gas flame* they impart a carmine-red coloration to the flame. In order to obtain the reaction with silicates containing lithium, an addition of plaster of Paris or, better, of a mixture of plaster of Paris and pure fluor spar in the proportion of 2 : 1 is required. Lithium phosphate gives the flame coloration on moistening the fused bead with hydrochloric acid. The lithium coloration is masked by the sodium coloration, and must, therefore, in the presence of sodium compounds be viewed through blue glass or through thin layers of indigo solution. A little potassium does not mask the lithium flame; in the presence of much potassium lithium may be detected by introducing the substance into the fusion area of the flame, and comparing the colour produced with that given by pure potassium when the flame is viewed through an indigo prism (see p. 92). When seen through the thinner layers of the prism the lithium flame appears redder than the potassium flame, but through somewhat thicker layers the flame

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[1] *Zeitsch. anal. Chem.*, **29**, 232.

eventually appear of equal redness, when the proportion of lithium to potassium is very small; if the lithium predominates in the substance the intensity of the red lithium flame decreases perceptibly when viewed through the thicker layers, whereas the colour of the pure potassium flame is not weakened to any appreciable extent. By this means it is possible to detect fractions of one per cent. of lithium in potassium salts. Sodium salts, unless present in overwhelming quantity, have but little influence on these processes (Cartmell, Bunsen).

The *lithium spectrum* (Table I.) is particularly distinct. It is especially characterised by a beautiful carmine-red line α 670·82$\mu\mu$; less conspicuous is the faint orange-yellow line β 610·38$\mu\mu$. *The flame of a Bunsen burner* with ordinary gas as a rule shows only these lines, but if lithium chloride is introduced into a *hydrogen flame*, the temperature of which is higher, a faint blue line 460·24$\mu\mu$ appears, and this is intensified in the *oxyhydrogen flame*. Its position nearly coincides with that of the fainter of the two blue cæsium lines (Tyndall, Frankland).

8. For the *microchemical* methods of detecting lithium ion, see Haushofer, *Mikroskopische Reaktionen*, p. 89; Behrens-Kley, *Mikrochem. Analyse*, 3rd ed., p. 45; Schoorl, *Zeitsch. anal. Chem.*, **48**, 598.

Summary and Remarks.

In order to detect small quantities of cæsium, rubidium, and lithium ions in the presence of large quantities of sodium or potassium ions, as is necessary, for example, in the analysis of mineral waters, the dry chlorides are moistened with a few drops of hydrochloric acid and extracted with 80 per cent. alcohol, which leaves the greater proportion of the sodium and potassium chloride in the residue. The solution is evaporated to dryness, the residue [1] taken up with a little water, and an excess of platino-hydrochloric acid added The precipitate is separated by filtration, and repeatedly boiled with small quantities of water, in order to eliminate potassium platinochloride, as far as possible, and is tested with the spectroscope. For this purpose a small quantity of the precipitate is wrapped in a small piece of moistened filter paper, and round this is twisted a piece of fine platinum wire The paper is carbonised at the point of the flame, care being taken to avoid too high a temperature, and is then introduced into the fusion area of the flame placed in front of the slit of the spectroscope. Under these conditions the potassium spectrum gradually fades, whilst the cæsium and rubidium spectra, if these ions were present, become visible.

The filtrate from the platinochloride precipitate is treated with a little oxalic acid, and evaporated to dryness, the residue gently ignited to decompose sodium platinochloride and the excess of platino-hydrochloric acid, and moistened with hydrochloric acid, which is subsequently evaporated, and the lithium chloride finally extracted by means of a mixture of absolute alcohol and ether.[1] On evaporating this solution the lithium chloride is left in nearly pure condition, and can be submitted to further tests. Before drawing a conclusion as to the presence of lithium from the flame coloration, it is necessary to make sure, in order to prevent a mistake, that strontium and calcium ion are not present.

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[1] If alkali chlorides separated from silicates, such as lepidolite, are present, the treatment with alcohol may be omitted.

The above-described addition of hydrochloric acid before extracting the lithium chloride with alcohol is necessary, because lithium chloride, even on moderate ignition, is converted by the action of water vapour into lithium hydroxide, which then absorbs carbon dioxide from the air, forming lithium carbonate, which is insoluble in alcohol.

Lithium chloride may be separated from large amounts of sodium and potassium chlorides by decomposing the concentrated solution of the salts with fuming hydrochloric acid and decanting the solution containing the lithium chloride and traces of other chlorides from the precipitated chlorides of sodium and potassium.

SECOND GROUP

Cations of the Alkaline Earths.

Barium, Strontium, Calcium, Magnesium (Radium).

SEC. 33

Characteristics of the Group.

Position of the Members in the Periodic System. The second group contains the (unpaired) members occupying the left hand side of the second division of the periodic system (with the exception of beryllium) and also magnesium, which also belongs to the second group of the periodic system These comprise all the divalent elements: magnesium, Mg, calcium, Ca, strontium, Sr, barium, Ba, and radium, Ra Radium, the detection of which is effected with the aid of physical methods, need not be considered here; in its chemical behaviour it stands remarkably close to barium. The other elements have received the group name of "alkaline earth metals," owing to the fact that their oxides have long been known as "alkaline earths" As in the case of the first group there are also here three elements closely resembling each other calcium, strontium, and barium —whilst magnesium (analogous to sodium in the first group) stands somewhat apart. It is in many respects related to aluminium, which occupies an adjoining position in the same horizontal series of the periodic system. All members of the second group are strongly electro-positive, to an extent decreasing from barium to magnesium. The solubility of their oxides, or hydroxides, decreases in the same order of the series. All the hydroxides are strongly dissociated in aqueous solution, and are therefore to be described as strong bases. Their solutions accordingly show an alkaline reaction (in the case of the sparingly soluble magnesia the alkaline reaction is most plainly shown by bringing the substance into contact with moistened test paper).

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[1] Instead of a mixture of alcohol and ether, which can also be used for the separation of lithium chloride from potassium chloride, Gooch (*Zeitsch anal Chem.*, **26**, 355) recommends amyl alcohol; L. W. Winkler (*ibid*, **52**, **627**) isobutyl alcohol; Kahlenburg and Krauskopf (*Chem. Zentralbl.*, 1908, II, 982), and also Muhrmann (*Zeitsch. anal. Chem.*, **50**, 171), pyridine. Lithium chloride is easily soluble in these solvents, whilst the chlorides of the other alkali metals are practically insoluble therein.

Analytical character of the Group.—The normal carbonates and phosphates and the monohydrogen phosphates of the alkali metals dissolve with difficulty in water. (In so far as they dissolve the carbonates undergo hydrolytic dissociation and show an alkaline reaction.) Hence the salts of the alkaline earth metals are precipitated from their solutions by carbonates, phosphates, and monohydrogen phosphates of the alkali metals. This behaviour distinguishes the ions of the second group from those of the first. From the ions of the following groups, however, they are distinguished by the fact that they are not precipitated from their solutions either by hydrogen sulphide or ammonium sulphide. The oxides, hydroxides, and salts of the alkaline earth metals are white or colourless, in so far as they are not coloured by the anion, and are not volatile. The nitrates or chlorides are not precipitated from their solution by barium carbonate.

SPECIAL REACTIONS OF MEMBERS OF THE SECOND GROUP.[1]

SEC. 34.

(a) **Barium**, Ba, 137.37.

1. *Barium* is a divalent silvery-white (or according to other statements a golden-yellow) metal of sp. gr. 3.78 to 4.00. Its melting point is about 850°. It oxidises in the air (frequently with ignition). *Barium oxide* (baryta), BaO, is white, fuses at a strong white heat, and only volatilises at a very high temperature. When moistened with water it emits heat, and is converted into white *barium hydroxide*, $Ba(OH)_2$. This melts at a red heat, without liberating water, which, however, is set free on stronger ignition (Brügelmann). It is fairly soluble in hot but is somewhat sparingly soluble in cold water; it is readily dissolved by dilute hydrochloric or nitric acid.

2. *Barium salts* are, *for the most part, practically insoluble* in water. The soluble salts show a neutral reaction; with the exception of barium chloride, bromide, and iodide, they are decomposed when heated in an ignition tube. The insoluble salts, with the exception of barium sulphate and silicofluoride, are dissolved by dilute hydrochloric acid. *Barium chloride* dissolves with great difficulty, and barium nitrate is practically insoluble in *cold absolute alcohol*, whilst both salts are *practically insoluble* in a mixture of equal parts of *absolute alcohol* and *ether;* they do not deliquesce in the air. Barium nitrate and barium bromide are almost insoluble in amyl alcohol. Barium salts in concentrated solution are precipitated by the addition of a large amount of hydrochloric or nitric acid, owing to the fact that the increase in the concentration of the anions causes the respective solubility products to be exceeded, since the saturation concentrations of the undissociated molecules of barium chloride and nitrate are relatively low (*cf.* p 33).

3. **Ammonia** produces *no* precipitate in aqueous solutions of barium salts. **Potassium hydroxide** or **sodium hydroxide** (free from carbonate) only produce a precipitate when the solutions of barium salts are very concentrated. Water redissolves any such voluminous precipitate of *barium hydroxide crystals*, $Ba(OH)_2 + 8H_2O$

4 The **carbonates** of **alkali metals** and **ammonium** precipitate *barium carbonate*, $BaCO_3$, in the form of a white precipitate from solutions of barium salts. If the solution was acid the precipitation does not take place until after heating, because the hydrocarbonate ion, which is first formed, retains a corresponding quantity of barium ion in solution, until it has itself been decomposed Ammonium chloride dissolves the precipitate to a slight but appreciable extent; hence no precipitate is formed in very dilute solutions containing much ammonium chloride.[1]

5. **Sulphuric acid** and *sulphate solutions*, including the **calcium sulphate (plaster of Paris)** solution, *produce even in very dilute solutions of barium salts a heavy finely pulverulent precipitate of barium*

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[1] The solvent action of ammonium salts of strong acids in this and analogous cases, upon precipitates already formed, depends upon the fact that the ammonium salts undergo hydrolytic dissociation, whereby, since ammonium hydroxide is a weak base (see Sec. 30, 1), the hydrogen ion concentration is increased. In the case above-mentioned the carbonate ion concentration is thereby reduced, with the formation of hydrocarbonate ions, or also of carbon dioxide. This reduction of a factor of the solubility product (Ba][CO''_3] is then equalised by solution of a part of the precipitate. In addition to this, there is also a repression of the dissociation of the ammonium carbonate through the presence of the ammonium ions of the neutral salt. These two processes supplement or overlap each other to a certain extent.

sulphate, $BaSO_4$. As a rule, the precipitate forms immediately; only in very dilute solutions, especially when strongly acid, is a certain time required for its appearance. The precipitate is *insoluble* in alkali hydroxide solutions, and is only *very slightly soluble in dilute acids*, but dissolves to an appreciable extent in concentrated hydrochloric or nitric acid, especially on heating, as also in concentrated solutions of salts of ammonium, potassium, sodium, calcium, and magnesium. The solvent action of acids and of solvents is inhibited, or at all events very much weakened, when sulphuric acid or sulphates are present in considerable excess. The presence of foreign salts has an influence upon the action in the way described on p. 34. Hence the solubility product of barium sulphate is not exceeded until there is a high concentration of barium and sulphate ions. If still more sulphate ions are present this disturbing influence of foreign salts is again repressed, *i.e.* the solubility product is then exceeded at a lower concentration of barium ions. Large amounts of calcium chloride may entirely inhibit the precipitation of small quantities of barium ions by calcium sulphate (Ludeking[1]), because the calcium chloride keeps the dissociation of the calcium sulphate, *i.e.* the concentration of the sulphate ions, below the quantity required to reach the solubility product of barium sulphate.

6. **Silicohydrofluoric acid** *precipitates from solutions of barium salts a colourless crystalline precipitate of barium silicofluoride*, $BaSiF_6$, which rapidly subsides. In dilute solutions the precipitate is only produced after some time. No precipitate is formed in very dilute solutions, for barium silicofluoride is not insoluble in water. On adding an equal volume of alcohol the precipitation takes place rapidly and so completely that the filtrate remains clear on the addition of sulphuric acid. Hydrochloric and nitric acids, as also ammonium salts, increase the solubility of the precipitate in water and in alcohol. In using the reaction it is necessary to take into consideration the fact that silicohydrofluoric acid also yields precipitates with potassium and sodium ions, so that, unless these ions are known to be absent, the presence of barium ion cannot be positively inferred from the occurrence of a precipitate.

7. **Disodium hydrogen phosphate** *produces in neutral or alkaline solutions a white precipitate of barium monohydrogen phosphate*, $BaHPO_4$, which is soluble in free acids. The addition of ammonia only increases the amount of the precipitate to a slight extent, a portion of it being converted into normal barium phosphate,

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[1] *Zeitsch. anal. Chem.*, **29**, 556.

$Ba_3(PO_4)_2$. Ammonium chloride dissolves the precipitate to an appreciable extent.

8 **Ammonium oxalate** *produces in moderately dilute solutions of barium salts a white pulverulent precipitate of barium oxalate*, $BaC_2O_4+H_2O$, which is soluble in hydrochloric and nitric acids. When freshly precipitated this compound is also dissolved by oxalic and acetic acids But these solutions soon yield a deposit of barium hydrogen oxalate, $BaH_2(C_2O_4)_2+2H_2O$, in the form of a crystalline powder

9 **Potassium chromate and dichromate** *produce in solutions of barium salts*, even when considerably diluted, *a pale yellow precipitate of barium chromate*, $BaCrO_4$ This dissolves with difficulty in cold water, more readily in boiling water; ammonium salts increase the solubility very appreciably, whilst acetic acid and chromic acid increase it considerably. Barium chromate is readily soluble in hydrochloric and nitric acids, whilst ammonia reprecipitates it from the resulting reddish yellow solution.

The solubility of barium chromate is also greatly increased by the presence of hydrogen ions, since chromic acid in its secondary stage is a weak acid (see p. 33 *et seq*), and $Cr_2O''_7$ ions are also formed (*cf.* Sec 101). The precipitation of barium by means of potassium dichromate is, therefore, by no means complete, even in the case of neutral solutions of barium salts, since hydrogen ions are formed in accordance with the equation: $2Ba^{\cdot\cdot}+Cr_2O''_7+H_2O$ $2BaCrO_4+2H^{\cdot}$. *But the addition of sodium acetate in excess causes the precipitation to be complete*, because then the hydrogen ion combines with the anion of the weak acid to form an undissociated acid molecule (not acting as an acid). (See p 25)

$2Ba^{\cdot\cdot}+Cr_2O''_7+H_2O+2CH_3COO'=2BaCrO_4+2CH_3COOH$; for example, $2BaCl_2+K_2Cr_2O_7+H_2O+xCH_3COONa=2BaCrO_4+2KCl+2NaCl+2CH_3COOH+(x-2)CH_3COONa$

A similar effect is produced by an excess of potassium dichromate. In this case only the CrO''_4, and not the $Cr_2O''_7$, is active By adding an excess of sodium acetate to acid solutions of barium salts prior to the addition of potassium chromate, or by adding to such acid solutions so much potassium dichromate that the whole of the chromate ion is not at once converted into dichromate ion, the *precipitation is rendered complete*

10. **Potassium ferrocyanide solution** *produces in concentrated solutions of barium salts a crystalline precipitate of barium potassium ferrocyanide*, $BaK_2Fe(CN)_6+3H_2O$. In the presence of ammonium

salts barium-potassium-ammonium ferrocyanides of variable composition are precipitated. The precipitate is also not insoluble in excess of potassium ferrocyanide solution, and hence this reagent does not effect a complete precipitation; *no precipitation is produced in dilute solutions.*

11. **Sodium sulphite** (freshly prepared concentrated solution) produces in solutions of barium salts a white precipitate of *barium sulphite*, $BaSO_3$, which is insoluble in acetic acid and dilute hydrochloric acid. (H. J. D. Hinds, *Chem. Zentralbl*, 1911, I., 1556)

12. *Barium sulphate* is not, or strictly speaking, is hardly decomposed by cold solutions of *alkali hydrogen carbonates* or *ammonium carbonate*, and the same remark applies to a boiling solution of 1 part of *potassium carbonate* and 3 parts of *potassium sulphate*. It behaves towards these reagents, however, in quite a different way when it is mixed with strontium or calcium sulphates (see p. 156 *f.*). Boiling solutions of *alkali carbonates* when repeatedly applied eventually decompose barium sulphate completely. **Fusion with alkali carbonates** readily decomposes it; alkali sulphate, soluble in water, and barium carbonate, insoluble in water, are formed.

13. *When barium salts are introduced on a platinum wire into* **the fusion area of a Bunsen flame,** *the portion of the flame above the substance is coloured yellowish-green* Soluble barium salts and also barium carbonate and sulphate show the reation at once or very soon, whilst the phosphate does not show it until after moistening with sulphuric or hydrochloric acid This last method may also be used for detecting barium in silicates which can be decomposed by acids, silicates which are not decomposed by acids, however, must be fused with sodium carbonate. The resulting barium carbonate then shows the reaction It is characteristic of the greenish-yellow coloration of the barium flame that it appears bluish-green when viewed through a green glass. Calcium and strontium do not prevent the barium reaction when the sulphate is used for the test. The yellowish-green flame reaction can also be obtained by mixing the powdered barium salt with alcohol and igniting the latter.

The **barium spectrum** is shown in Table I. The green lines α $524\mu\mu$, β $513{\cdot}2\mu\mu$, and δ $553{\cdot}5\mu\mu$ are the most intense, whilst γ $582{\cdot}5\mu\mu$ is less prominent but yet characteristic.

Since commercial platinum wire may contain barium (Kraut), it is advisable to see whether the wire alone does not give a barium spectrum.

14. For the *microchemical detection* of barium reference may be made to Haushofer, *Mikroskopische Reaktionen*, p. 15; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 58; Schoorl, *Zeitsch. anal. Chem.*, **48**, 403.

SEC. 35.

(b) **Strontium,** Sr, 87·63.

1. *Strontium* is a divalent silvery-white, or, according to other statements, yellow metal, of sp. gr. 2·50 to 2·58. It melts at 800°. It closely resembles barium in its behaviour. In like manner its *oxide* (*strontia*), SrO, its *hydroxide*, and its salts show almost exactly the same properties as the corresponding barium compounds.

Strontium hydroxide is less soluble than barium hydroxide, and only loses its water after strong ignition. *Strontium chloride* is not soluble in the anhydrous condition in anhydrous alcohol; but if it contains its water of crystallisation (as in the case of the residue obtained on evaporating the solutions) it *is soluble in absolute alcohol*, and deliquesces on exposure to moist air; it is also soluble in strong hydrochloric acid. Strontium bromide is soluble in ethyl alcohol and in amyl alcohol.

Strontium nitrate is *almost insoluble in absolute alcohol*, *practically insoluble* in a mixture of equal parts of *absolute alcohol and ether*, and quite insoluble in concentrated nitric acid. Strontium nitrate does not deliquesce on exposure to the air.

2. Strontium salts behave in almost exactly the same way as barium salts towards **ammonia, potassium hydroxide,** and **sodium hydroxide,** as also towards the **carbonates of the alkali metals** and of **ammonium,** and towards **disodium hydrogen phosphate.** *Strontium carbonate* is *less* soluble than barium carbonate in ammonium chloride solutions.

3. **Sulphuric acid** and **sulphates** *produce in not too dilute solutions of strontium salts* a white precipitate of *strontium sulphate*, $SrSO_4$. As precipitated from concentrated solutions this is at first amorphous and flocculent, and later pulverulent and crystalline; precipitated from dilute solutions it is pulverulent and crystalline at once. Heat greatly accelerates the precipitation. Strontium sulphate is much more soluble in water than the corresponding barium compound, for which reason the precipitate is only formed after some time in more dilute solutions. **Calcium sulphate solution** precipitates strontium immediately only from quite concentrated and especially hot solutions of strontium salts, *whilst* it only produces a precipitate after some time from more dilute solutions. Potassium, sodium, calcium, and

magnesium salts increase the solubility of strontium sulphate so that, *e.g.* in presence of much calcium chloride, strontium ion is not precipitated by calcium sulphate solution (Ludeking). Strontium sulphate is appreciably soluble in hydrochloric and nitric acids. The presence of any large amount of these acids therefore affects the sensitiveness of these reactions to a remarkable extent. An excess of sulphuric acid counteracts the solvent action of these salts and acids (see Sec. 34, 5). *Strontium sulphate is not soluble, even on boiling, in a concentrated solution of ammonium sulphate,* but if mixed with calcium sulphate dissolves to a considerable extent simultaneously with the latter.

4. **Silicohydrofluoric acid** produces *no* precipitate even in fairly concentrated solutions of strontium salts, since strontium silicofluoride, $SrSiF_6$, is fairly soluble in cold water; hot water dissolves it somewhat less readily, so that hot concentrated solutions yield a precipitate It is slightly soluble in *dilute* alcohol, the solubility decreasing with the increase in the alcoholic strength. The addition of alcohol therefore effects a precipitation even in the cold Hydrochloric acid increases very greatly the solubility of the salt in water, and its solubility in alcohol to a somewhat less extent.

5. **Ammonium oxalate** *produces, even in fairly dilute solutions* of strontium salts, a white *pulverulent precipitate* of *strontium oxalate*, $2SrC_2O_4 + 5H_2O$, which dissolves readily in hydrochloric acid and nitric acid, fairly readily in solutions of ammonium salts, but is only slightly soluble in oxalic acid solution and acetic acid.

6. **Potassium dichromate** does *not* produce a precipitate even in concentrated solutions of *strontium salts*, nor does **potassium chromate** at first. In the latter case, however, a light yellow precipitate of *strontium chromate*, $SrCrO_4$, separates after some time, from not too dilute neutral solutions (more rapidly from ammoniacal solutions), but not from solutions acidified with acetic acid. The precipitate is in the form of a fine powder, which adheres to the sides of the vessel (Reichard [1]). It is only sparingly soluble in water containing much ammonia or acetic acid, but is readily soluble in hydrochloric, nitric, and chromic acids. It is not precipitated from its solution in any of these by the addition of potassium dichromate in excess. Alcohol does not dissolve strontium chromate Neutral solutions of strontium salts mixed with potassium chromate therefore yield a precipitate on adding a small amount of alcohol. The precipitation is promoted by heating the liquid to 70° (W. Fresenius and Ruppert [2]).

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[1] *Zeitsch. anal. Chem.*, **46**, 178.

[2] *Ibid.*, **30**, 672.

7. **Potassium ferrocyanide** *does not precipitate strontium from solutions of its salts.*

8. *Sodium sulphite* (freshly-prepared concentrated solution) precipitates white *strontium sulphite* from neutral or acetic acid solutions, but not from hydrochloric acid solutions of strontium salts (Hinds[1])

9 *Strontium sulphate* is *decomposed* in the cold when treated with solutions of *carbonates of potassium and sodium ;* it is also completely decomposed by a longer treatment with cold solutions of *ammonium carbonate* or of *potassium* or *sodium hydrogen carbonates*, and much more rapidly when boiled with a solution of 1 *part of potassium carbonate* and 3 *parts of potassium sulphate.* In these decompositions (except those effected by potassium and sodium carbonate) a certain amount of strontium sulphate always remains undecomposed when it was originally mixed with barium sulphate. The decomposition is also effected rapidly and completely by fusing or boiling the sulphate with alkali carbonates.

10 *When a solid strontium compound is introduced into the fusion area of a* **Bunsen flame** *an intense red flame coloration* is produced Strontium chloride shows this reaction most clearly, strontium oxide and carbonate less distinctly, strontium sulphate still more slightly, and the salts of acids not decomposed on heating very faintly, if at all The substance is therefore first tested by itself and then after moistening with hydrochloric acid If the presence of strontium is suspected, the substance is heated for a short time in the reducing flame (to produce strontium sulphide) before it is moistened with hydrochloric acid When viewed through a blue glass the strontium flame appears purple to rose colour (distinction from calcium compounds, which under these conditions show a faint greenish-grey coloration), the coloration is most distinct when the substance is moistened with hydrochloric acid and sprayed into the flame In the presence of barium compounds the strontium reaction appears when the substance moistened with hydrochloric acid, is first introduced into the flame The carmine-red flame coloration may also be produced by heating soluble strontium salts with dilute alcohol and igniting the vapour

The **Strontium spectrum** is shown in Table I. It contains many characteristic lines, notably the orange line α 605·5$\mu\mu$, the red lines β 679·7$\mu\mu$, and γ 649·9$\mu\mu$, and the blue line δ 460·7$\mu\mu$. The last is particularly suitable for the detection of strontium in the presence of barium and calcium

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[1] *Chem. Zentralbl.*, 1911, I., 1556.

11. For details of the microchemical detection of strontium, see Haushofer, *Mikroskopische Reaktionen*, p. 121; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 54; Schoorl, *Zeitsch. anal. Chem.*, **48**, 404.

SEC. 36.

(c) Calcium, Ca, 40.07.

1. *Calcium* is a divalent silvery-white (yellowish when not quite pure) metal, with sp. gr. 1.52 and melting point 810°. It oxidises in the air, forming calcium hydroxide and carbonate, and decomposes water, with the liberation of hydrogen and formation of calcium hydroxide. *Calcium oxide* (lime), CaO, and the hydroxide and salts of calcium closely resemble in general properties the corresponding compounds of barium and strontium. *Calcium hydroxide*, $Ca(OH)_2$, is far less soluble in water than the hydroxides of barium and strontium, and is less soluble in hot than in cold water. Calcium hydroxide loses its water on ignition.

The *chloride* and *nitrate of calcium* are *soluble* in *absolute alcohol* and in a mixture of *equal parts of alcohol and ether*; they deliquesce on exposure to the air. The nitrate is also (relatively) fairly soluble in strong nitric acid, and the chloride in strong hydrochloric acid.

2. **Ammonia, potassium hydroxide, sodium hydroxide,** and the **carbonates and phosphates of the alkali metals** *behave towards calcium salts in nearly the same way as towards barium salts.* Freshly precipitated *calcium carbonate*, $CaCO_3$, is voluminous and amorphous, but after standing some time, or immediately on heating, it agglomerates and becomes crystalline. The freshly-formed precipitate dissolves fairly readily in ammonium chloride solution, but the solution soon becomes turbid and deposits the greater part of the dissolved salt in crystalline form.

3. **Sulphuric acid and sodium sulphate** *produce immediately in quite concentrated solutions of calcium salts a white precipitate of calcium sulphate* (gypsum), $CaSO_4 + 2H_2O$, which dissolves completely in a large volume of water, and is still more soluble in acids. In less concentrated solutions of calcium salts the precipitate only forms after standing for some time, whilst *still more dilute solutions do not yield a precipitate.* Naturally, calcium sulphate cannot produce a precipitate, whilst a cold solution of potassium sulphate, diluted with 3 parts of water, only produces a precipitate after 12 to 14 hours in solutions of calcium salts. If solutions of calcium salts are so dilute that sulphuric acid by itself does not yield a

precipitate, *an addition of an equal volume, or better, of twice the volume of alcohol will cause one to appear immediately*, or, in the case of very dilute solutions, after some time. Calcium sulphate dissolves in a sufficient quantity of a concentrated solution of ammonium sulphate, but only completely when there is no admixture of barium or strontium sulphate.

4 **Silicohydrofluoric acid** does *not* precipitate calcium from solutions of its salts, when an equal volume of alcohol is added.

5 **Ammonium oxalate** *produces in solutions of calcium salts a white pulverulent precipitate of calcium oxalate.* If the solution is concentrated or hot, the precipitate $CaC_2O_4 + H_2O$ is formed immediately, but if it is very dilute and cold the precipitate is only formed after some time, and is then distinctly crystalline, and consists of a mixture of the above salt with $CaC_2O_4 + 3H_2O$. Calcium oxalate is readily soluble in hydrochloric or nitric acid, but is not appreciably so in acetic acid or oxalic acid solution

6 **Potassium chromate** *at first produces no precipitate* even in concentrated neutral solutions of calcium salts Only after standing for a long time does *calcium chromate*, $CaCrO_4 + 2H_2O$, separate as a yellow crystalline precipitate But on adding 2 to 3 volumes of *alcohol an immediate precipitation takes place* in the case of solutions which are not too dilute The addition of a sufficient quantity of ammonia to even somewhat dilute solutions of calcium salts which have been treated with potassium chromate also causes a precipitate to form (Reichard[1]) Free acetic acid and the addition of alcohol prevent the precipitation of calcium by potassium chromate from solutions of its salts **Potassium dichromate** does not produce a precipitate even in concentrated solutions.

7 **Potassium ferrocyanide** *produces in solutions of calcium salts a white crystalline precipitate of calcium potassium ferrocyanide*, $CaK_2Fe(CN)_6 + 3H_2O$. In the presence of ammonium salts calcium potassium ammonium ferrocyanides of variable composition are precipitated The precipitate is so insoluble in presence of an excess of potassium ferrocyanide that the filtrate remains clear on the addition of ammonium oxalate (Baubigny,[2] Flanders[3]).

8. *Sodium sulphite* (in freshly prepared saturated solution) produces *no precipitate* in solutions of calcium salts acidified with hydrochloric or acetic acid (Hinds[4]).

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[1] *Zeitsch. anal. Chem*, **46**, 178.
[2] *Chem. Zentralbl.*, 1895, I., 1040; 1907, II, 663.
[3] *Ibid.*, 1906, II., 1873.
[4] *Ibid*, 1911, I., 1556.

9. *Barium fluoride* produces in solutions of calcium salts a colourless or white precipitate of *calcium fluoride*, CaF_2. (Distinction from barium and strontium). By this test 0·8 mgrm. of calcium chloride can be detected in 10 c.c. of solution. The presence of barium salts in considerable quantities has an influence on the reaction (Karaoglanoff [1]).

10. Calcium sulphate behaves in the same manner as strontium sulphate on adding *carbonates* or *hydrocarbonates of alkali metals* or a mixture of *potassium carbonate and sulphate* to its solution, or when it is fused with alkali carbonates.

11. *Calcium salts*, when introduced into the **fusion area of the Bunsen flame** *produce a yellowish-red flame coloration*. Calcium chloride shows the reaction most distinctly, whilst calcium sulphate only shows it after it has begun to decompose; it is also most distinct in the case of calcium carbonate after the carbon dioxide has escaped The salts of acids which stand the heat of the flame do not colour the flame, but do so after they have been moistened with hydrochloric acid so as to decompose them. The best method is to heat a small quantity of the substance on platinum wire, to add a drop of hydrochloric acid so that it remains suspended from the loop of the wire, which is then introduced into the fusion area of the flame. The reaction appears most distinctly at the moment when the drop disappears without boiling (as in Leidenfrost's phenomenon) (Bunsen). The calcium coloration of the flame, when produced by spraying the substance moistened with hydrochloric acid into the flame, appears, when viewed through a green glass, of a yellowish-green colour (Distinction from strontium, which under the same conditions yields a fugitive yellow coloration) (Merz). In the presence of barium, the reaction only appears when the substance moistened with hydrochloric acid is introduced just into the flame.

Soluble calcium salts when heated with alcohol produce a flame with a yellowish-red colour. It is difficult to distinguish with certainty between calcium and strontium by means of the flame coloration.

The **calcium spectrum** is shown in Table I. It is particularly characterised by the intense green line β 558·9$\mu\mu$, and by the intense orange double line α 643·9 646·2$\mu\mu$; the indigo-blue line 422·6$\mu\mu$, not far from the Fraunhofer line *G*, is only visible in very good apparatus, because it emits less light.

12. For the *microchemical reactions* of calcium, see Haushofer,

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[1] *Zeitsch. anal. Chem.*, **56**, 138.

Mikroskopische Reaktionen, p. 32; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 49; Schoorl, *Zeitsch. anal. Chem.*, **48**, 409.

SEC. 37.

(d) Magnesium, Mg, 24·32.

1. *Magnesium* is a divalent metal. It is silvery-white, hard, malleable, of sp. gr. 1·743; it melts at a moderate red heat (below 800°) and volatilises at a white heat. When heated in the air it burns with a dazzling white flame, forming *magnesium oxide* (magnesia), MgO. In dry air it keeps its lustre, but in moist air it gradually becomes coated with magnesium hydroxide. Pure water is not decomposed at the ordinary temperature by magnesium, but the metal dissolves easily and rapidly in water acidified with hydrochloric or sulphuric acid, with the liberation of hydrogen.

2. The *oxide* and *hydroxide* of magnesium are white powders, far more voluminous than the corresponding compounds of the other alkaline earth metals. They are hardly soluble in either cold or hot water. On ignition *magnesium hydroxide*, $Mg(OH)_2$, decomposes water.

3. Some *magnesium salts* are soluble and others insoluble in water. The soluble salts have an unpleasant bitter taste, have a neutral reaction (at all events in the case of the neutral salts, p. 7) towards indicators, and are, with the exception of the sulphate, decomposed on gentle ignition. In certain circumstances they are decomposed on evaporating their solutions, in consequence of hydrolysis and evaporation of the liberated volatile acids (*e.g.* the chloride in concentrated solution). At a strong white heat magnesium sulphate is also decomposed with the liberation of sulphur trioxide. The insoluble magnesium salts are almost all dissolved readily by hydrochloric acid.

4. **Ammonia** *precipitates from neutral solutions of magnesium salts free from ammonium ion a portion of the magnesium ion in the form of a white flocculent deposit of magnesium hydroxide*, $Mg(OH)_2$. The precipitate is *soluble* both in *acids* and in *solutions of ammonium salts*. If, therefore, the solution contains such salt, or if on neutralising any acid present ammonium ions are produced in the liquid, *no precipitation will take place*. (For the explanation of this behaviour, see p. 33.)

Since under all conditions there is a formation of ammonium ions in the solution during the precipitation process, the checking of the dissociation of the (slightly basic, see Sec. 30, 1) ammonium hydroxide has a restrictive influence upon the precipitation of the remainder of the magnesium ions. Hence in no case can a complete precipitation of the magnesium ion be effected by means of ammonia.

This property is utilised for keeping magnesium ion in solution while other metal ions are being precipitated by means of ammonia, ammonium sulphide, or ammonium carbonate. In such cases a sufficient quantity of ammonium chloride is added, and no precipitation of a magnesium compound is then produced by means of ammonia (or ammonium sulphide or carbonate).

5. **Potassium, sodium, barium, and calcium hydroxides** *precipitate magnesium hydroxide from solutions of magnesium salts. Ammonium chloride* and similar ammonium salts cause the freshly-precipitated and well-washed hydroxide to redissolve. If they are added in sufficient quantity to the solution of magnesium salt prior to the addition of the precipitant no precipitate is obtained on the addition of a little alkali. It is not until the quantity of alkali is so great that a sufficient number of hydroxyl ions is present that the solubility product is exceeded and precipitation takes place. This is naturally promoted by boiling. The presence of chlorides or sulphates of potassium and sodium also checks the dissociation of the hydroxides of these metals. Hence magnesium hydroxide appears to be more soluble in solutions of these alkali salts than in water, or in other words, magnesium ion is less completely precipitated by small amounts of alkali hydroxides when neutral salts of alkali metals are present in the solution. From such solutions, however, magnesium ion is precipitated, for the most part, by an excess of potassium or sodium hydroxide

6. **Potassium or sodium carbonate** *produce in neutral solutions of magnesium salts a white precipitate of basic magnesium carbonate,* $[4MgCO_3+Mg(OH)_2+xH_2O]$.[1] *A further atom* remains in solution as magnesium ion, together with the hydrocarbonate ions, which have been formed. That is to say, there is a hydrolytic dissociation of two of the six molecules of magnesium carbonate :

$$6Mg^{\cdot\cdot}+6CO''_3+2H_2O=[4MgCO_3+Mg(OH)_2]+Mg^{\cdot\cdot}+2HCO'_3$$

for example,

$$6MgCl_2+6Na_2CO_3+2H_2O \\ =4MgCO_3+Mg(OH)_2+Mg(HCO_3)_2+12NaCl$$

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[1] The composition (*i.e.* the relative proportions) of $MgCO_3$ and $Mg(OH)_2$ may vary somewhat with the conditions of the precipitation.

On boiling the liquid carbon dioxide is expelled, and a further precipitate, $MgCO_3+H_2O$, is produced:

$$Mg^{\cdot\cdot}+2HCO'_3=MgCO_3+H_2O+CO_2$$

Hence, heating the liquid promotes the precipitation of magnesium by alkali carbonates and increases the quantity of the precipitate. *Ammonium chloride* and similar *ammonium salts* may, when present in sufficient quantity, also prevent this precipitation, or cause the washed precipitate to dissolve readily. The same conditions are then produced as if ammonium carbonate had been directly added (see 7).

7. *If a solution of a magnesium salt is treated with* **ammonium carbonate** *the liquid always remains clear at first.* On standing, however, there separates (rapidly from concentrated and more slowly from dilute solutions) *a crystalline precipitate*, which consists of magnesium carbonate, $MgCO_3+3H_2O$, when a small amount of ammonium carbonate was added and of ammonium magnesium carbonate, $Mg(NH_4)_2(CO_3)_2+4H_2O$, when a larger amount was added. Only when the solutions are very dilute is no precipitate formed. The addition of ammonia or of ammonium carbonate in excess has a strong influence in promoting the precipitation; *ammonium chloride* has the opposite effect, but does not prevent the precipitation in the case of more concentrated solutions. The checking or prevention of the precipitation depends upon the restrictive action of the ammonium ions of other ammonium salts upon the dissociation of the ammonium carbonate (see 5, and footnote 1, p. 139).

8. **Disodium hydrogen phosphate** *precipitates magnesium monohydrogen phosphate*, $MgHPO_4+7H_2O$, *as a white powder from not too dilute solutions of magnesium salts.* On boiling, *normal magnesium phosphate*, $Mg_3(PO_4)_2+7H_2O$, separates even from fairly dilute solutions. But if **ammonium chloride and ammonia** *are added to the solution of magnesium salt prior to the addition of the disodium hydrogen phosphate*, there is produced, even in a very dilute solution, *a white crystalline precipitate* of ammonium magnesium phosphate, $Mg(NH_4)PO_4+6H_2O$.[1] In the case of very dilute solutions the separation of the precipitate is promoted by stirring the liquid with a glass rod. If the dilution is so great that a precipitate no longer forms, the lines made by the glass rod upon the sides of the vessel in

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[1] The magnesium hydrogen phosphate precipitate is also converted into this compound on the subsequent addition of ammonium chloride.

stirring the liquid become visible after some time as white streaks, removable by hydrochloric acid. Water and solutions of ammonium salts have hardly any solvent action on the precipitate, but acids and even acetic acid dissolve it readily. It is practically insoluble in ammoniacal water. **Ammonium sodium hydrogen phosphate** may, of course, be used instead of disodium hydrogen phosphate; in that case magnesium ammonium phosphate is always precipitated.

9. **Ammonium oxalate** *does not produce a precipitate in very dilute solutions;* in less dilute solution no precipitate is formed at first, but after standing for some time crystalline aggregations of various ammonium magnesium oxalates are formed at the edges of the surface of the liquid. In *quite concentrated* solutions of magnesium salts ammonium oxalate speedily produces precipitates of *magnesium oxalate*, $MgC_2O_4+2H_2O$, which contain small amounts of the above-mentioned double salt. Ammonium chloride and free ammonia interfere with the formation of these precipitates, but, as a rule, do not entirely prevent it.

10. **Potassium ferrocyanide** does not produce a precipitate immediately in cold dilute solutions of magnesium salts, but a white crystalline precipitate separates, on standing, more rapidly in the case of concentrated solutions. Heating accelerates the precipitation and renders it complete. The precipitate is *magnesium potassium ferrocyanide*, and, in the presence of ammonium salts, *magnesium potassium ammonium ferrocyanide*.

11. **Sulphuric acid, silicohydrofluoric acid and potassium chromate** produce *no* precipitates in solutions of magnesium salts.

12. Magnesium salts do not impart *any coloration to a flame* (*cf.*, however, the end of Sec. 38).

13. If magnesium chloride or nitrate solution is added to an *alcoholic tincture of alkanet* (prepared by treating powdered alkanet root with 93 per cent. alcohol) and the mixture made alkaline, the liquid shows a characteristic *absorption spectrum*, the principal band of which corresponds with the wave length $606{\cdot}3\mu\mu$, whilst fainter bands correspond with wave lengths $561{\cdot}1\mu\mu$ and $521{\cdot}3\mu\mu$. The reaction is very sensitive. It may also be used for the detection of magnesium ion in the presence of alkali ions or those of barium, strontium, or calcium. If large amounts of these are present the absorption bands appear somewhat displaced towards the red end. Magnesium ion may also be detected in this way in the presence of ferric ion; but it is necessary to make the observation immediately after the addition of the ammonia, since ferric hydroxide is

precipitated and carries down with it an appreciable quantity of magnesium (Formanek[1]). For particulars of the detection of magnesium by *absorption spectrum analysis* with the aid of *purpurin*, see also Vogel and v. Lepel[2]

11. For the *microchemical detection* of magnesium reference may be made to Haushofer, *Mikroskopische Reaktionen*, p. 92; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 42; Schoorl, *Zeitsch. anal. Chem.*, **48**, 594; Vivario and Wagenaar, *Chem. Zentralbl.*, 1917, II., 211.

SEC. 38.

Summary and Remarks on Group II.

1. The three principal points which distinguish the *magnesium ion* from the ions of the other alkaline earth metals are the sparing solubility of magnesium hydroxide, the ready solubility of magnesium sulphate (when not present as kieserite the form of magnesium sulphate of natural occurrence containing one molecule of water), and the fact that the presence of ammonium salts prevents the precipitation of magnesium ion by ammonia or ammonium carbonate. To detect the magnesium ion in solutions, which may also contain the ions of all the alkaline earth metals, barium, calcium, and strontium ions, if present, are first removed. This is most suitably done by precipitation in the form of carbonates (which leaves these ions in the form of compounds suitable for further examination). In order to avoid a simultaneous precipitation of magnesium carbonate or hydroxide the solution is first treated with so much ammonium chloride that it remains clear on the addition of ammonia to alkaline reaction, and is then treated with sufficient ammonia to make the reaction distinctly alkaline and with ammonium carbonate. Finally, the liquid is gently heated. If the solution is fairly dilute, and is filtered after about an hour, the carbonates of barium, strontium, and calcium are left upon the filter (for their separation, *vide infra*), whilst the whole of the magnesium remains in solutions and will be found in the filtrate. But since ammonium chloride solution dissolves a certain amount of barium carbonate, and also, though to a less extent, of calcium carbonate, small amounts of the ions of these metals will be present in the filtrate—and, in fact, if only traces were originally present, may remain entirely in the solution. In complete investigations the filtrate is, therefore, divided into three parts, one of which is treated with a few drops of sulphuric acid for the detection

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[1] *Zeitsch. anal. Chem.*, **39**, 414.

[2] *Ibid.*, **17**, 89.

of the dissolved trace of *barium ion*, and the second with ammonium oxalate, so that any small quantity of *calcium ion* remaining in solution may not be overlooked. If neither reagent produces any turbidity, even after some time, the third portion of the filtrate is tested for magnesium ions by means of disodium hydrogen phosphate. If, on the other hand, one of the reagents produces a turbidity, the precipitate, which gradually subsides, is filtered off before applying the test for magnesium ion, and should both reagents cause turbidities the two portions are mixed, the mixture, which must still be alkaline, is filtered after some time, and the filtrate tested for magnesium ion.

To prove that a precipitate really consists of calcium oxalate, and not of ammonium magnesium oxalate, it is dissolved in hydrochloric acid, and the solution treated with sulphuric acid and alcohol, which, in the presence of calcium ion, produce a precipitate.

2. The above-mentioned **carbonate precipitate,** which may contain *barium*, *strontium*, and *calcium*, is thoroughly washed to remove the magnesium ion, which might interfere with the subsequent separation of the other alkaline earth metals. Various methods may be used for the detection of barium, strontium, and calcium in the precipitate

(*a*) The precipitate is dissolved in acetic acid, the solution evaporated on the water-bath until the bulk of the acetic acid has been removed, and then diluted with water, and the liquid, which must still be perceptibly acid (if not, a few additional drops of acetic acid are added), is treated with potassium chromate until it shows a yellow colour, and heated to boiling point. If any odour of acetic acid is still perceptible a little more potassium chromate solution is added.

If barium ion is present it is precipitated completely as barium chromate. The liquid is allowed to stand for about an hour, and then filtered. The filtrate (which must not contain more than 10 per cent of calcium or strontium salts, or calcium ion may be precipitated with the strontium ion) is treated with ammonia (free from carbonate) until of a pale yellow colour, when an additional 10 drops of ammonia solution are added, and the liquid is treated with an equal quantity of a mixture of 2 parts (by volume) of 93 per cent. alcohol and 1 part of water. (Care must be taken that both the ratio between the volumes of solution and dilute alcohol, and the prescribed dilution of the latter are fairly closely maintained) If *strontium ion* is present a *yellow precipitate* is obtained. (Heating promotes its separation, but the temperature must not exceed 60°–70°.)

The liquid is filtered and the filtrate treated with *potassium ferrocyanide* solution (not too concentrated, or potassium ferrocyanide will be precipitated by the alcohol) and gently heated if a precipitate has not already been formed in the cold. If *calcium ion* is present a white precipitate of *calcium potassium ferrocyanide* is formed.[1]

(*b*) The carbonates are dissolved in acetic acid, and the *barium ion* precipitated with *potassium chromate*, as described in (*a*). The filtrate from the barium chromate precipitate is neutralised with ammonia and the carbonates of strontium and calcium precipitated with ammonium carbonate. After standing for a long time the precipitate is dissolved in the smallest possible amount of hydrochloric acid, the carbon dioxide expelled by boiling, and the solution neutralised with ammonia, and, after the addition of a little ammonium chloride solution, treated with an equal volume of a saturated solution of *potassium ferrocyanide* and heated to boiling point. Calcium ion is precipitated as calcium potassium ammonium ferrocyanide This is separated by filtration, and the filtrate is treated with ammonium carbonate Strontium carbonate is precipitated, but only after a considerable time when the quantity is small The presence of strontium ion is confirmed by dissolving the separated precipitate in hydrochloric acid, evaporating the solution to dryness, dissolving the residue in a little water and adding calcium sulphate solution.

(*c*) The carbonates are dissolved in dilute nitric acid, and the solution evaporated on the water-bath to dryness, the residue heated somewhat more strongly (not over 180°) on an asbestos plate, the *dry nitrates* powdered and mixed in a dry boiling flask with a mixture of equal parts of *absolute alcohol and ether*, and the flask corked and allowed to stand for some time with frequent shaking.

Calcium nitrate dissolves, whilst, if the nitrates were quite dry, *barium and strontium nitrate remain undissolved* The precipitate is filtered off and washed four times with a mixture of equal parts of absolute alcohol and ether. The filtrate is treated with a *few drops of dilute sulphuric acid*. Since calcium sulphate is insoluble in alcohol a *precipitate* must be formed in the presence of *calcium ion*. If any appreciable amount of precipitate is produced the presence of calcium ion is indicated. If it is only small, it may be due to a slight quantity of strontium sulphate derived from strontium nitrate, which, if water has not been completely excluded, may have dissolved. In this case the solution is mixed with about 4 c.c. of water, the ether and alcohol evaporated, a few drops of ammonia solution and about 1 grm. of solid ammonium sulphate added, and the liquid heated to boiling point and filtered. The filtrate is treated with one drop of acetic acid, so as just to redden litmus paper, and then with a few drops of *ammonium oxalate solution.* If *calcium ion* is present a precipitate of calcium oxalate is formed immediately, or after standing for some time if the quantity is small. This cannot be mistaken for strontium ion, which may be present in small quantity, since the traces of strontium sulphate, which dissolve in a concentrated solution of ammonium sulphate, are not precipitated by ammonium oxalate in presence of free acetic acid.

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[1] With regard to other suggestions for methods of separation based upon the different degrees of solubility of the chromates, see Dumesnil, *Zeitsch. anal. Chem*, **41**, 695; Reichard, *ibid.*, **46**, 178.

The undissolved *nitrates of barium and strontium* are dissolved in 70 to 100 times their weight of water, the solution filtered, boiled if necessary to remove the alcohol and ether, and acidified with a few drops of acetic acid, and the *barium ion* precipitated with potassium chromate, as described above under (*a*). The filtrate is tested for *strontium ion* with *ammonium carbonate*, as described at the end of (*b*). A small precipitate, which might be due to insufficiently washed calcium nitrate, is dissolved in hydrochloric acid and tested with calcium sulphate solution, as in (*b*), or the hydrochloric acid solution is neutralised with ammonia, boiled to remove carbon dioxide, and treated with potassium chromate and dilute alcohol, as in (*a*).

(*d*) The barium ion may also be precipitated, as in (*a*), and the strontium and calcium ions, as in (*b*), as carbonates, the precipitate dissolved in nitric acid, and the nitrates separated by means of ether-alcohol, as in (*c*).

(*e*) *Small quantities of calcium ion* in the presence of a *large amount of barium and strontium ions* may also be detected by treating the solution with a little hydrochloric acid, heating it, adding dilute *sulphuric acid*, filtering off the precipitate, and first rendering the filtrate alkaline with ammonia, then acidifying it with acetic acid, and adding *ammonium oxalate.* A precipitate, which is often only produced after a considerable time, indicates calcium ion, since traces of strontium sulphate, which may have remained in solution during the precipitation with sulphuric acid, are not precipitated by ammonium oxalate from solutions containing free acetic acid.

(*f*) The older methods commonly used for the separation of barium, strontium, and calcium ion, or for the detection of one ion in the presence of one of the others, which were based on the difference in their behaviour towards calcium sulphate solution, on the separation of the dry chlorides by means of alcohol, and on the separation of the sulphates of strontium and calcium by means of ammonium sulphate, are much less accurate than those described, as may be gathered from what has been said about the reactions of the individual ions.

Nor is the method of separating barium ion from strontium ion, based upon the different behaviour of the sulphates towards a solution of ammonium carbonate, or a mixture of potassium carbonate and sulphate, to be recommended, since when barium sulphate predominates a portion of the strontium sulphate remains undecomposed, whilst when the strontium sulphate predominates barium sulphate is also converted into carbonate. This method of separating barium and strontium ion gives better results than the preceding ones, but is also not exact. The methods of separating the nitrates and chlorides depending upon their different solubility in concentrated nitric acid, which does not dissolve barium and strontium nitrate (S. G. Rawson, *Zeitsch. anal. Chem.*, **46**, 178), or in concentrated hydrochloric acid, which does not dissolve barium chloride, but dissolves the chlorides of strontium and calcium (E. Ebler, *Zeitsch. anal. Chem.*, **48**, 175), are unpleasant to use. We may also refer to a method of detecting and separating barium, strontium, and calcium ions, which Hinds [1] has based upon the difference in solubility of the respective *sulphites* in hydrochloric acid, acetic, acid and water (Sec. 31, 11; Sec. 35, 8, and Sec. 36, 9).

3. *If sulphates of the alkaline earth metals* are under examination, the mixture may first be extracted with a small quantity of water. The solution will contain the whole of the magnesium sulphate, when the latter is not present in the form of kieserite, together with a small amount of the calcium sulphate. The residue is fused with 4 parts of potassium and sodium carbonates, the fused mass treated with boiling water, the extract filtered, and the insoluble carbonates washed and separated by one of the methods described above (under 2).

Phosphates of the alkaline earth metals may be decomposed by means of ferric chloride, with the addition of sodium acetate (see Phosphoric acid, Sec. 107, 9); the respective oxalates are differentiated by converting them into carbonates by ignition, whilst the fluorides and silicofluorides are first converted into sulphates by heating them with concentrated sulphuric acid.

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[1] *Chem. Zentralbl.*, 1911, I, 1556.

4. Barium, strontium, and calcium ion may be detected much more easily, even when they are all present together, by means of the flame coloration observed through a *spectroscope*, than by the above-described somewhat tedious wet methods, which, however, also afford an approximate estimation of the relative quantities. According to the anion present, the substance is either introduced directly into the flame, or is so introduced after ignition in the reducing flame and moistening with hydrochloric acid.

If very small amounts of barium and strontium are to be detected in the presence of a large amount of calcium, a few grms of the carbonates are strongly ignited in a platinum crucible over the blow-pipe flame (in which process the carbonates of barium and strontium are more readily converted into oxides in the absence of calcium carbonate), the ignited mass boiled with a little water, the solution filtered and evaporated to dryness, and the residue examined with the spectroscope (Engelbach).

If traces of calcium and strontium are to be detected in barium minerals, they are converted by a suitable method into chlorides, the latter extracted with a very small amount of absolute alcohol, the extract evaporated, and the residue examined with the spectroscope.

For the detection of traces of calcium and barium in strontium minerals, the chlorides are repeatedly extracted first with cold and then with hot alcohol. The first extract will contain the calcium, the later ones the strontium, and the final extract or residue the barium. In each case the substance is ignited in the reducing flame, then moistened with hydrochloric acid, and introduced into the spectroscope flame (Bunsen).

Good results are sometimes obtained by the use of the lamps devised by Beckmann[1] (*cf.* Sec. 22, p. 98), in which the salt is distributed through hydrogen and introduced together with the gas into the flame. A similar appliance has also been devised by E. H. Riesenfeld and H. E. Wohlers.[2]

E. H. Riesenfeld and G. Pfutzer (*Ber.*, **46**, 4130) recommend the use of *arc-light spectra* for the spectroscopic detection of the members of the second analytical group, and describe a special apparatus for the production of such spectra. By this means it is possible to detect not only barium, strontium, and calcium, but also magnesium, the spectrum of which under these conditions shows three adjacent lines, 516·8, 517·3 and 518·1.

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[1] *Zeitsch. physik. Chem.*, **57**, 649. [2] *Ber.*, **39**, 2628; *Chem. Zeit.*, **30**, 704.

THIRD GROUP.

Ions of the Metals of the Earths.

Members of frequent occurrence: **Aluminium, Chromium.**

Members of rarer occurrence: **Beryllium, Thorium, Zirconium, Yttrium (and other ions of the yttria earths), Cerium, Lanthanum, Didymium** (*Praseodymium and neodymium*), **Scandium, Titanium, Tantalum, Niobium.**

SEC. 39.

Characteristics of the Group.

Position of the Members in the Periodic System.—The only elements of frequent occurrence contained in the third analytical group are *aluminium*, the characteristic member of the third group of the periodic system and *chromium*, which occupies quite a different position in the periodic system (in the sixth group), but which, in so far as it is present as chromic ion, $Cr^{\cdot\cdot\cdot}$, closely resembles aluminium in its analytical behaviour. On the other hand, the elements of rarer occurrence classified in this group are very numerous. Of these, beryllium, which heads the list of the second group of the periodic system, is in accordance with the general analogies of the system, closely related to aluminium. To this group also belong all the members, following scandium, titanium, or niobium, of the left-hand sub-group of the third, fourth, and fifth groups of the periodic system. The elements termed in the more restricted sense *metals of the rare earths*, are, with the exception of cerium, only trivalent; in accordance with their occurrence and behaviour they are grouped under the collective name of metals of the yttria or ceria earths, and recently, with the exception of scandium and yttrium, which both have quite different atomic weights, and accordingly have their own place in the periodic system, they are frequently placed together in the positions occupied by lanthanum and cerium (p. 115).[1] This also gives expression to the fact that these elements have a particularly close resemblance to each other, and that some of them cannot be separated at all by the ordinary analytical methods. They are all, including cerium in its trivalent form, strongly electro-positive, and as regards their basicity come between magnesium and aluminium; hence they have only a slight tendency to form complexes and to undergo hydrolysis.

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[1] *Cf.* Brauner, *Zeitsch. anorgan. Chem.*, **32**, 1; R. J. Meyer, *Naturwissenschaften*, **2**, 781.

The tetravalent elements belonging to the fourth group of the periodic system, titanium, zirconium, and thorium, as also cerium in its tetravalent oxidation state, are essentially more electro-negative, and of these zirconium and thorium may also be grouped with the metals of the rare earths in the wider signification. But, even in the fourth group of the periodic system, the positive character increases with the rise in atomic weight, so that, whilst titanium shows an amphoteric behaviour, and is found both in combination with oxygen as the *anion* of a weak acid (especially in alkaline fused masses) and also as the *cation* of a weak base (in acid aqueous solution), thorium is known only as cation, and there are no thorates corresponding to the titanates The solution of the salts all show a strong tendency to hydrolyse and be converted into the colloidal condition, and this again is most pronounced in the case of titanium which also has the greatest tendency to form complexes.

The two elements, niobium and tantalum, belonging to the fifth group of the periodic system, are, in their normal pentavalent condition, decidedly negative (formation of anions). Their salt solutions usually undergo pronounced hydrolysis and readily assume the colloidal condition

Analytical Characters of the Group. *The oxides, hydroxides, and salts of oxygenated acids of metals of the third group do not volatilise on ignition. The oxides, hydroxides, and phosphates are insoluble in water.* The hydroxides usually show a considerable tendency to form colloidal solutions. In accordance with their weak electro-positive character, as compared with that of members of the two preceding groups, the members of this group *show no tendency to form carbonates* The sulphides cannot be prepared by the wet method *Hydrogen sulphide*, therefore, does *not* form a precipitate in the solutions of their salts. *Ammonium sulphide*, like *ammonia*, precipitates the *hydroxides* from solutions of salts containing the metals of the third group as cations (With regard to their occurrence as anions in combination with oxygen and organic groups, *vide infra*). *This behaviour towards ammonia and ammonium sulphide distinguishes the metals of the third group from those of the preceding groups.*

Nearly all the metals of the third group can both form salts with acid radicles (in the solutions of which they are thus present as cations), and can also combine with oxygen to form acid radicles (anions), which then unite with strongly basic cations to form salts, so that in that case the metals of the third group are part of the anion. The hydroxides of metals of the third group can therefore act both as bases and as acids. In the case of the last three members of the group the hydroxides (and in the older nomenclature their anhydrides, the oxides) are, therefore, also termed *acids*, because they are already of a pronounced acid character. Some of the metals of the third group can form complex compounds with hydroxylated organic substances. *In the presence of such organic substances* these metals are contained in solutions of their salts, not as cations, but as constituents of *complex anions, and hence do not show the ordinary reactions, e.g. are not precipitated by alkali hydroxides.*

SPECIAL REACTIONS OF THE MEMBERS OF GROUP III. OF FREQUENT OCCURRENCE.

SEC. 40.

(a) **Aluminium**, Al, 27·1.

1. *Aluminium* occurs as a constituent of rocks, especially as silicate, and is very widely distributed in all kinds of soil. It is a trivalent, nearly white metal of sp. gr. 2·583, and melts at 654·5°. It does not oxidise when exposed to the air, and in compact masses hardly does so, even on ignition. It is prepared by electrolysing the oxide between carbon electrodes in an electric furnace. It can be filed and is very ductile. Aluminium does not decompose water even at the boiling point. It dissolves readily in hydrochloric acid with the liberation of hydrogen, forming aluminium chloride, $AlCl_3$, and also in warm potassium hydroxide solution, forming potassium aluminate, $Al(OK)_3$ or $AlO.OK$; it is only slowly dissolved by nitric acid, even on heating.

2. *Aluminium oxide* (alumina), Al_2O_3, does not volatilise on ignition, and, like the hydroxide, $Al(OH)_3$, is white or colourless. It dissolves slowly and very sparingly in dilute acids, but somewhat more readily in hot concentrated hydrochloric acid. Fusion with potassium hydrogen sulphate converts it readily into a mass which is soluble in water. In the amorphous condition the *hydroxide* is readily soluble in acids, but in the crystalline condition dissolves with very great difficulty therein. After ignition with alkalis or alkali carbonates the resulting alkali aluminate is readily dissolved by acids. By igniting a mixture of alumina and carbon in a current of chlorine, or by the action of carbon tetrachloride vapour, CCl_4, or alumina at a temperature below red-heat (Demarcay), a sublimate of aluminium chloride, $AlCl_3$, is obtained.

3. *Aluminium salts* are white or colourless, those containing

oxygen are non-volatile, some are insoluble, others soluble. Anhydrous aluminium chloride is solid, forms colourless crystals, is volatile, and dissolves easily in water. The soluble aluminium salts of oxygenated acids have a sweet taste, coalesce, redden litmus (owing to hydrolytic dissociation), and decompose on ignition into aluminium hydroxide and the so-called acid anhydride. The salts insoluble in water are, with the exception of certain compounds of natural occurrence, dissolved by hydrochloric acid; those insoluble in hydrochloric acid are decomposed on ignition with sodium and potassium carbonates or potassium hydrogen sulphate (p. 57). They may also be decomposed and dissolved by heating them for 2 hours at 200° to 210° in a finely powdered condition with 25 per cent. hydrochloric acid, or with a mixture of 3 parts by weight of concentrated sulphuric acid and 1 part of water in sealed glass tubes (A. Mitscherlich).

4. **Potassium hydroxide and sodium hydroxide** (as also barium and calcium hydroxides) *produce in solutions of aluminium salts a voluminous precipitate of aluminium hydroxide*, $Al(OH)_3$ (containing alkali and usually mixed with basic salt), *which is readily and completely soluble in excess of the precipitating reagent.* The solution of aluminium hydroxide in solutions of the hydroxides mentioned depends upon the fact that it is an amphoteric electrolyte (*i.e.* positive or negative according to the conditions). When the hydroxyl ion concentration is sufficiently high (excess of alkali hydroxide) hydrogen ion is split off from the portion of aluminium hydroxide remaining in solution as base (and combines with the hydroxyl ion to form water), and the cation $Al^{\cdots}$ is thus converted into the anion AlO'''_3 or $AlO.O'$:

$$(Al^{\cdots}+3OH')+(3OH'+3Na^{\cdot})=(AlO'''_3+3Na^{\cdot})+3H_2O$$

or

$$(Al^{\cdots}+3OH')+(OH'+Na^{\cdot})=(AlO.O'+Na^{\cdot})+2H_2O\quad,$$

This destroys the equilibrium between the undissolved aluminium hydroxide (the body substance) and the aluminium hydroxide remaining in solution as base, so that a further portion of aluminium hydroxide is dissolved, and undergoes the same decomposition. This process continues, in presence of a sufficient excess of alkali hydroxide, until the whole of the aluminium hydroxide has dissolved. The process of the conversion of $Al^{\cdots}+6OH'$ into $AlO'''+3H_2O$ is reversible, and only continues to finality from left to right when there is a great excess of hydroxyl ions. The solution of the resulting alkali aluminate remains clear on boiling, but the aluminium hydroxide is re-precipitated even in the cold, and completely on boiling, by the addition of ammonium chloride. This precipitation by ammonium chloride depends upon the fact that ammonium ion is decidedly less positive than sodium or potassium ions, and also in aqueous solution is largely decomposed into ammonia NH_3 and hydrogen ion $H^{\cdot}$, which combines with hydroxyl ion to form water. This causes a pronounced reduction in the hydroxyl ion concentration, and the anion AlO''' or $AlO.O'$ is re-converted into the cation $Al^{\cdot\cdot\cdot}$ and the hydroxyl ion (*i.e.* the process described above runs from right to left). If the solubility product of aluminium and hydroxyl ions is thereby exceeded, aluminium hydroxide is precipitated. On heating the liquid the volatilisation of ammonia reduces the hydroxyl ion concentration still further, and thus makes the precipitation more complete. *The precipitate is not soluble in excess of ammonium chloride solution. Ammonium salts do not interfere with the precipitation of aluminium hydroxide by potassium or sodium hydroxide.* Acids first precipitate aluminium hydroxide from solutions of alkali aluminate, and when added in further quantity re-dissolve the precipitate. The reactions outlined proceed as follows:—

$$Al^{\cdot\cdot\cdot}+3OH'=Al(OH)_3$$

$$Al(OH)_3+3OH'=AlO'''_3+3H_2O$$

or $$Al(OH)_3+OH'=AlO.O'+2H_2O$$

e.g. $$AlCl_3+3KOH=Al(OH)_3+3KCl$$

$$Al(OH)_3+3KOH=Al(OK)_3+3H_2O$$

or $$Al(OH)_3+KOH=AlO.OK+2H_2O$$

and in the reverse direction:

$$AlO'''_3+3H^{\cdot}=Al(OH)_3$$

or $$AlO.O'+H^{\cdot}+H_2O=Al(OH)_3$$

$$Al(OH)_3+3H^{\cdot}=Al^{\cdot\cdot\cdot}+3H_2O$$

e.g. $$Al(OK)_3+3HCl=Al(OH)_3+3KCl$$

or $$AlO.OK+HCl+H_2O=Al(OH)_3+KCl$$

$$Al(OH)_3+3HCl=AlCl_3+3H_2O$$

The precipitation of aluminium hydroxide from aluminate solutions by means of ammonium salts is shown in the equation:

$$AlO'''_3+3NH^{\cdot}_4=Al(OH)_3+3NH_3$$

e.g. $$Al(ONa)_3+3NH_4Cl=Al(OH)_3+3NaCl+3NH_3$$

5. **Ammonia,** and also **ammonium sulphide,** *both produce a precipitate of aluminium hydroxide* (containing ammonia and basic salt). This is dissolved, with the formation of aluminate, on adding a considerable excess of ammonia, but not readily, the difficulty of solution increasing with the proportion of ammonium salts in solution

(*i.e.* the more the dissociation of the ammonium hydroxide is checked). Boiling promotes the precipitation by causing the excess of ammonia to escape.

6. **The carbonates of alkali metals and ammonium** *produce a white, flocculent precipitate,* the composition of which varies with the conditions of concentration and temperature. It is a strongly basic aluminium carbonate or a mixture of much aluminium hydroxide with some aluminium carbonate. The aluminium carbonate formed in the equation :

$$2Al^{\cdots}+3CO''_3=Al_2(CO_3)_3$$

e.g. $$2AlCl_3+3Na_2CO_3=Al_2(CO_3)_3+6NaCl$$

is, to a large extent, immediately hydrolysed :

$$2Al^{\cdots}+3CO''_3+6H_2O=2Al(OH)_3+3H_2CO_3$$

The unstable carbonic acid molecule then decomposes with the formation of water, and *carbon dioxide which escapes with effervescence.* The precipitate is somewhat soluble as aluminate in excess of potassium or sodium carbonate solution, but less so in excess of ammonium carbonate solution. In the case of the latter boiling promotes the precipitation.

7. On treating the solution of an aluminium salt with finely divided **barium carbonate** (precipitated in water) *decomposition takes place even on standing in the cold. Barium ion is dissolved while aluminium is precipitated as a basic salt or hydroxide and carbon dioxide escapes.*

8. *Sodium thiosulphate solution gives, on heating, a white precipitate, consisting of a mixture of aluminium hydroxide and sulphur.* (According to Friedheim and Zimmermann the precipitate also contains basic aluminium sulphate and sulphite.)

The reaction takes place in accordance with the equation :

$$2Al^{\cdots}+3S_2O''_3+3H_2O=2Al(OH)_3+3S+3SO_2$$

e.g. $$2AlCl_3+3Na_2S_2O_3+3H_2O=2Al(OH)_3+6NaCl+3S+3SO_2$$

Here, owing to the hydrolytic dissociation of the aluminium salt, the resulting free acid (*i.e.* its hydrogen ion) has a decomposing action upon the thiosulphate ion :

$$S_2O''_3+H^{\cdot}=HSO'_3+S$$

The weakly negative hydrosulphite ion combines with a further hydrogen ion to form undissociated sulphurous acid, which decomposes, especially on heating, to form water and sulphur dioxide, which escapes. As the hydrogen ion corresponding with the hydrolysis equivalent:

$$(Al^{\cdot\cdot\cdot}+3Cl')+3(H^{\cdot}+OH')\rightleftarrows(Al^{\cdot\cdot\cdot}+3OH')+3(H^{\cdot}+Cl')$$

is removed, a new dissociation of the aluminium salt continually takes place, the solubility product of aluminium hydroxide is exceeded, and the hydroxide is precipitated.

Notes to 4, 5, 6, 7, and 8: (*a*) If *phosphate ion* is also present in the aluminium solution, phosphate, not hydroxide, is precipitated. (*b*) *Tartaric acid*, *citric acid*, and other non-volatile organic acids, if present to any considerable extent, interfere with the precipitation of aluminium, owing to the formation of complex anions. For the same reason the presence of sugar and similar organic substances has an influence on the completeness of the precipitation.

9. **Disodium hydrogen phosphate** *precipitates aluminium phosphate*, $AlPO_4+4H_2O$, *from solutions of aluminium salts*. The voluminous precipitate dissolves readily in potassium and sodium hydroxide solutions, with the formation of aluminate ion, AlO'''_3, and phosphate ion, PO'''_4, but with more difficulty in ammonia solution, and is almost insoluble in the presence of ammonium salts. Hence ammonium chloride precipitates it from solutions containing sodium or potassium hydroxide. The precipitate is readily soluble in hydrochloric or nitric acid, but not in acetic acid (distinction from aluminium hydroxide); sodium acetate therefore precipitates it from its solution in hydrochloric acid, if the latter is not too concentrated. Tartaric acid, sugar, etc., do not interfere with the precipitation of aluminium phosphate, but citric acid prevents it (Grothe).

10. **Oxalic acid** and its salts do *not* precipitate aluminium from solutions of its salts.

11. *Potassium sulphate*, when added to very concentrated solutions of aluminium salts, causes a gradual separation of *aluminium potassium sulphate* (alum), $AlK(SO_4)_2+12H_2O$, in the form of crystals or a crystalline powder. Analogous alums are also produced by other members of the first analytical group, especially rubidium and cæsium ion. Use is made of the sparing solubility of the cæsium alum in the microchemical detection of aluminium.

12. *On igniting aluminium compounds on charcoal by means of* the blowpipe, *then moistening the deposit with a solution of* **cobaltous nitrate,** and again igniting it strongly, *an unfused bright blue mass* (a cobalto-aluminate) is obtained. The colour first appears distinctly

after cooling. In candle light it appears violet. The reaction is only relatively distinctive when the blue mass is infusible or melts with difficulty ; it is never absolutely decisive, because there are not only readily fusible compounds free from aluminium, but also some which fuse with difficulty or not at all (*e g.* the neutral phosphates of the alkaline earths), which can give a blue coloration when ignited with cobaltous solution.

13. Alkanet tincture [1] is gradually coloured reddish-violet with strong orange-yellow fluorescence by neutral solutions of aluminium salts (chloride or nitrate). The solution shows a *characteristic absorption spectrum* with three bands at $585{\cdot}75\mu\mu$, $512{\cdot}5\mu\mu$, and $504{\cdot}8\mu\mu$ respectively If the solution is too concentrated, so that the bands cannot be distinctly recognised, the solution is diluted with alcohol. In dilute solution the coloration at first develops gradually, and the bands recede by degrees from the places of lower to those of higher refrangibility Ammonia precipitates aluminium hydroxide, whilst nearly all the other metals give in ammoniacal solution more or less characteristic colorations and absorption spectra with alkanet tincture. Hence, as a rule, they do not interfere with the aluminium reaction. (Formanek, *Zeitsch anal. Chem* , **39**, 116) With regard to absorption spectra, see also H W. Vogel, *ibid.*, **15,** 332, and **17**, 89, and F. v. Lepel, *ibid* , **17**, 89.

14. *Morin solution* [2] gives a very fine green fluorescence with solutions of aluminium salts, even when greatly diluted. (Distinction from beryllium and the other rare earths.) (Goppelsroder, *Zeitsch. anal. Chem.*, **7,** 195.) With regard to the detection of aluminium by means of *logwood tincture*, see also Horsley and Schumacher-Kopp, *ibid.*, **31,** 222 ; by means of *cochenille tincture*, see Kuckow, *ibid* , **3,** 362 ; and by means of *alizarin*, see F. W. Atack, *Chem. Zentralbl.*, 1916, I., 176.

15. For the *microchemical detection* of aluminium, see Haushofer, *Mikroskopische Reaktionen*, p. 12 ; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 80 ; Schoorl, *Zeitsch anal. Chem.*, **48,** 215, and **50,** 266 ; Rathgen, *ibid.*, **53,** 33.

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[1] For the method of preparing this, see Magnesium, Sec. 37, 3.

[2] Morin is a dyestuff occurring in fustic. It is prepared by boiling the fustic repeatedly with water, and concentrating the filtrate, which causes calcium morin to separate. On treating this with sulphuric acid containing alcohol calcium sulphate is formed, and the morin remains in solution in the alcohol, from which it can then be precipitated by water. (Lowe, *Zeitsch. anal. Chem.*, **14,** 117). The above-mentioned reagent is an alcoholic solution of pure morin.

SEC. 41.

(b) Chromium, Cr, 52.

1. *Chromium* in the pure condition is a white, lustrous, crystalline, hard, brittle metal of sp. gr 6·92, melting at 1515° Chemically it is characterised by the fact that it shows very different stages of valency, which in some cases change easily into each other. In the compounds of most frequent occurrence it is either trivalent, and analogous to aluminium, as in *chromic* compounds (which are mainly dealt with in this section), or hexavalent, as in *chromates* (which are more fully described among the anions, Sec 101). In addition to these, there are also compounds of divalent chromium, *chromous* compounds, and tetravalent and pentavalent chromium, but they are not of frequent occurrence, and some of them, as, for example, the chromous compounds, which speedily absorb oxygen, are very unstable, they can easily be converted into chromic compounds or chromates and identified as such *Metallic chromium* is soluble in hydrochloric acid and other hydrogen halogen acids, in sulphuric acid and in oxalic acid solution, with the liberation of hydrogen and formation of chromic compounds (or mixtures of chromous and chromic compounds) It is insoluble in oxidising acids (nitric acid, chloric acid) and in weak acids (phosphoric acid, tartaric acid, etc) The solubility is greatly modified by various influences such as immersion in nitric acid, or anodic polarisation. Chromium which has been subjected to this treatment is no longer soluble in dilute acids, but retains its lustre on exposure to air and behaves as a "noble" metal. This is termed the "passive" condition of chromium, as distinguished from the "active" condition, in which the chromium dissolves in dilute acids and undergoes superficial oxidation on exposure to the air.

2 *Chromic oxide*, chromium oxide, Cr_2O_3, is an amorphous green powder, but also occurs in the form of nearly black crystals (green when powdered). The *hydroxide*, which can form hydrates with variable amounts of water, is usually a grey-green powder. The precipitated hydroxide, $Cr(OH)_3\ 2H_2O$, is readily soluble in acids. When dehydrated below ignition temperature it yields hydroxides containing less water and eventually the oxide. These compounds are only sparingly soluble in acids, and when ignited become incandescent, and are converted into a yellowish-green oxide insoluble in acids. Two different types of hydroxides correspond with the two series of salts (see 3), $Cr(OH)_3$, corresponding with the violet salts, and $CrO(OH)$ with the green salts.

3. The *chromic salts*, corresponding with chromic oxide, are usually violet in the crystalline condition. Many of them dissolve in water, and most in hydrochloric acid. The solutions of the salts are of a violet or green colour. When heated, the violet solutions become green, whilst on spontaneous evaporation of the green solution there is a gradual change back into the violet salt. On evaporating the violet solutions crystals are obtained, the green solutions yield either an uncrystallisable syrup or crystals of the violet compounds, into which they have been converted. The violet salts are to be regarded as the neutral salts, and the green salts as the basic salts, mentioned above as corresponding with the hydroxide (see 2). Hence they are produced in the solutions from the normal violet salts in consequence of a partial hydrolytic dissociation in accordance with the reaction: $Cr^{\cdot\cdot\cdot} + H_2O = CrO^{\cdot} + 2H^{\cdot}$. The formation of complex ions is also involved in the process[1] Chromium can also form complex compounds with a whole series of other substances, as, for example, with hydrocyanic acid, with sulphuric acid, with organic compounds containing hydroxyl, as well as with ammonia, amines, pyridine, etc. (chromiac compounds) These complex compounds do not show the reactions of the chromic ion. Chromic salts of volatile acids lose their acids on ignition; aqueous solutions of soluble salts redden litmus, owing to hydrolysis Anhydrous chromic chloride prepared by sublimation is crystalline, volatilises with difficulty, is violet in colour, and insoluble in water and acids The presence of even a small quantity of chromous chloride or a similar reducing agent renders anhydrous chromic chloride soluble.

4. **Potassium or sodium hydroxide** *produces both in the green and violet solutions of chromic salts a bluish-green precipitate of chromic hydroxide, which on addition of excess of the precipitant, forms chromite ions*, $CrO_3H'_2$ or CrO'''_3, *and dissolves readily and completely to an emerald green solution If this solution is boiled for some time, the precipitate* (unlike the compound in the corresponding aluminate solution) *separates completely*, so that the supernatant liquid appears completely colourless. The chromite ions are thus unstable at the boiling temperature. Hence the alkali hydroxide solutions of chromic hydroxide are frequently regarded as only colloidal solutions of the hydroxide. The decomposition of chromites on boiling takes place in accordance with the equations:

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[1] Recoura, *Bull. Soc. Chim.* [3], **6**, 909; Whitney, *Zeitsch. physik. Chem.*, **20**, 40.

$$CrO_3H'_2+H_2O=Cr(OH)_3+OH'$$

or $$CrO'''_3+3H_2O=Cr(OH)_3+3OH'$$

e.g. $$CrO_3H_2Na+H_2O=Cr(OH)_3+HaOH$$

or $$Cr(ONa)_3+3H_2O=Cr(OH)_3+3NaOH$$

5. **Ammonia,** and also **ammonium sulphide,** precipitates from green solutions of chromic salts grey-green *chromic hydroxide*, and from violet solutions grey-blue hydroxide The former precipitate is soluble in cold hydrochloric acid forming a red-violet solution, whilst the latter gives a bluish-violet solution Other conditions (such as the concentration, method of adding the ammonia, etc.) also have an influence on the composition and colour of these hydroxides. In the presence of excess of ammonia the hydroxides dissolve to a slight extent in the cold, forming a peach-coloured to deep red solution, but on boiling the resulting solution for some time the hydroxide is completely precipitated

6 *Sodium thiosulphate solution* produces, on boiling, a grey-green precipitate of *chromic hydroxide* and *sulphur* The remarks made in connection with the analogous reaction of aluminium compounds (See 10, 8) also apply to the formation of this precipitate

7. **Alkali carbonates** precipitate *basic chromic carbonate*, which is only sparingly and slowly soluble on adding excess of the precipitant (*cf* Sec 10, 6)

8. **Barium carbonate** *precipitates from solutions of chromic salts the whole of the chromic ion* in the form of *hydroxide* mixed with basic salt The separation takes place even in the cold, but is only complete after standing for a considerable time (*cf* Sec 40, 7).

9. **Disodium hydrogen phosphate** precipitates from boiling green or violet, neutral or slightly acid, chromic salt solutions, which have been treated with sodium acetate, the whole of the chromium as chromic phosphate, $CrPO_4+3H_2O$, in the form of a light green precipitate (A Carnot)

Notes to 4, 5, 7, 8, and 9: The precipitability of chromic ion by means of ammonia from solutions of either the violet or green chromic salts is more or less influenced by the presence of tartaric acid, citric acid, sugar, and oxalic acid, after standing for some time the precipitates first produced redissolve completely, forming violet or green solutions The precipitation by barium carbonate is inhibited by the presence of the above-mentioned acids. A solution of a chromic salt, which has been boiled for some time with sodium acetate, and then cooled, is not precipitated by alkali hydroxides and carbonates, barium carbonate, or ammonium sulphide in the cold, but gives a precipitation on boiling (Reinitzer).

10. On boiling a potassium or sodium hydroxide solution of chromic hydroxide for a short time with a slight excess of brown **lead peroxide** *the chromic ion is oxidised to chromate ion.* On filtration a yellow solution containing chromate and plumbate anions is obtained On acidification with acetic acid *lead chromate* separates as a yellow precipitate (Chancel).

11. If a liquid containing chromic ion is run into a hot solution of **sodium carbonate** containing **potassium permanganate,** and the mixture boiled for a short time, the chromic ion is converted into *chromate ion.* On then adding a few drops of alcohol to reduce the excess of permanganate, and filtering off the separated manganese dioxide hydrate, any appreciable quantity of chromium may be recognised by the yellow colour of the filtrate containing chromate ion (Donath)

Other oxidising agents, such as *bromine*, **hydrogen peroxide,** *sodium peroxide* (and also the *percarbonates*, *persulphates*, and *perborates* of the alkali metals) in alkaline solution also cause a change of chromic into chromate ion. This is indicated by the colour of the solution changing from green to yellow. Chromic ion may also be oxidised to chromate ion in acid solution, *e.g.* by means of *permanganate*, *nitric acid*, and *potassium chlorate*, or by means of ammonium persulphate in dilute sulphuric acid solution. In the presence of concentrated sulphuric acid the last reaction proceeds in the reverse direction (v. Knorre[1]).

12. If chromic oxide or a chromic salt is fused with *sodium nitrate* and *carbonate*, or better, with **potassium chlorate** and **sodium carbonate,** or with **sodium peroxide** (Hempel), the trivalent chromium is converted into the hexavalent condition. *Alkali chromate* dissolving in water to form an intense yellow solution is obtained by this reaction.

Notes to 10, 11, and 12: If the amount of chromium is so small that the filtrate does not show a yellow coloration, a trace of chromium present may often still be detected by concentrating the liquid and then applying the tests recommended for the detection of minute quantities.

13. **Alkali phosphate** dissolves chromic oxide and chromic salts both in the oxidation and reduction flame to form faint yellowish-green beads, the colour of which changes to emerald green on cooling. **Borax** behaves in a similar manner.

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[1] *Zeitsch. angew. Chem.*, **16**, 1098.

11 For the *microchemical detection* of chromic compounds, see Haushofer, *Mikroskopische Reaktionen*, p. 17; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 86; Schoorl, *Zeitsch. anal. Chem.*, **48,** 219.

SEC. 42

Summary and Remarks on Aluminium and Chromium.

Aluminium is characterised by the fact that it is precipitated by alkali (or barium) hydroxide, but redissolves on addition of excess of the reagent, and can be reprecipitated from this solution by means of ammonium chloride (or hydrochloric acid followed by ammonia).[1]

These characteristics, however, cannot be used for the detection of aluminium ion when chromic ion is simultaneously present, because the latter behaves in the same way. The alkaline solutions of aluminate ion and chromite ion may be distinguished, however, by the fact that the former is stable when boiled, whilst the latter is decomposed, with the precipitation of chromic hydroxide.

1. The ions of both metals of the third group may, therefore, be detected in solution by adding an excess of alkali hydroxide, diluting the clear alkaline solution with a suitable proportion of water, boiling it until the liquid is colourless, and then filtering it.

The green precipitate of chromic hydroxide is filtered off, and may be further identified, *e.g.* by means of phosphoric acid.

The filtrate is heated with a sufficient quantity of ammonium chloride, or, better, acidified with hydrochloric acid (which produces a temporary precipitate of aluminium hydroxide), and rendered just alkaline with ammonia. The gelatinous precipitate becomes flocculent on heating. It may be identified by its behaviour when heated with cobaltous nitrate in the blowpipe flame.

This method of separation is not always entirely trustworthy in the case of very small quantities of chromic ion. In the presence of non-volatile organic acids it fails altogether.

2. Hence the methods of separation based upon oxidation of the chromic ion to chromate ion are more certain. The oxidation may be effected in alkaline solution by boiling with potassium permanganate. The excess of the latter is reduced by heating the liquid with a

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[1] For the detection of traces of aluminium, C. H. Petit (*Chem. Zentralbl.*, 1914, I, 818) recommends that a hydroxide precipitate should first be produced by means of ammonia in the solution under examination, the liquid then treated with baryta water, heated to boiling point and filtered, and the filtrate acidified with sulphuric acid, filtered from the precipitated barium sulphate, and tested with ammonia.

little alcohol, and filtering it from the precipitated manganese dioxide hydrate. The yellow colour of the solution indicates the presence of chromium. On acidification the colour changes to reddish-yellow, owing to the formation of dichromate ion, and the aluminium ion may then be precipitated by means of ammonia.

Other oxidising agents, such as hydrogen peroxide or sodium peroxide, may be used instead of potassium permanganate. The alkaline (or if sodium peroxide has been used, slightly acidified) solution is boiled with the oxidising agent to destroy excess thereof, acidified and aluminium ion precipitated with ammonia. Chromic ion may also be oxidised in acid solution to chromate ion by means of potassium chlorate or ammonium persulphate, and aluminium ion finally precipitated as hydroxide.

If the acid solution containing chromic and aluminium ions is treated with sodium hydroxide until the precipitate first formed is completely re-dissolved, and bromine water then added in the cold until the colour of the liquid changes from green to yellow (until chromic ion has been converted into chromate ion), then heated to boiling point and treated with an excess of saturated bromine water, all the aluminate ion will be precipitated as hydroxide in accordance with the formula:

$$2Al(ONa)_3+3Br_2+3H_2O=2Al(OH)_3+NaBrO_3+5NaBr$$

(A temporary precipitate of chromic oxide may be produced on the first addition of bromine. Jakob, *Zeitsch. anal. Chem.*, **52,** 651.)

3. If *solid substances*, as *e.g.* the two oxides, are present, it is advisable to oxidise the chromium oxide by fusion with a flux.[1]

Thus, for example, 1 part of oxide is mixed with 2 parts of sodium carbonate and 2 parts of potassium chlorate,[2] and fused in a platinum crucible. After cooling, the mass is dissolved in water (the yellow colour indicates the presence of chromate ion), the solution filtered from the unaltered residue of aluminium oxide (which may be identified by heating it with cobaltous nitrate in the blowpipe flame). The filtrate is acidified with nitric acid, and the resulting reddish-yellow solution rendered alkaline with ammonia, which renders it yellow again, and precipitates in the form of hydroxide the remainder of the aluminium (*i.e.* the portion of the oxide which was converted into aluminate by the fusion, and on acidification was transformed from aluminate anion into aluminium cation) A certain amount of chromate ion may be carried down by the aluminium hydroxide (Brearley, *Chem. Zentralbl.* 1898, I., 1150).

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[1] Organic substances, if present, are best destroyed by ignition beforehand.

[2] Potassium chlorate is preferable to the nitrate, because the nitrite ion formed in the fusion process can again exert a reducing action on acidification.

If the substance is fused with sodium peroxide (with the necessary precautions)[1] or with a mixture of sodium peroxide and carbonate, the aqueous solution obtained by boiling the mass for some time with water (to destroy the peroxide) will contain the whole of the chromium as chromate ion, and all the aluminium as aluminate ion, and, after acidification, the aluminium ion may be precipitated with ammonia in the form of hydroxide.

SPECIAL REACTIONS OF THE RARER MEMBERS OF THE THIRD GROUP.[2]

SEC. 43.

1. Beryllium, Be, 9·1.

1. *Beryllium* is a divalent, white or greyish-white metal (sp. gr. 1·85, melting point below 1000°), which is stable in the air, does not decompose water, and is soluble in hydrochloric acid, sulphuric acid, and potassium and sodium hydroxide solutions, with the liberation of hydrogen. Beryllium is of rare occurrence in the form of a double silicate with aluminium in beryl and euclase, as a silicate in phenakite, and in some other rare minerals.

2. *Beryllium oxide* (berylla), BeO, is a white, tasteless powder insoluble in water. Prior to ignition it is readily soluble in acids, but after strong ignition dissolves slowly and sparingly in cold, but completely in hot, acids, and is readily soluble after fusion with potassium hydrogen sulphate. *Beryllium hydroxide*, $Be(OH)_2$, dissolves readily in acids when freshly precipitated, and is stable.

The *compounds* of beryllium closely resemble the compounds of aluminium. The soluble salts have a sweet astringent taste, and owing to hydrolytic dissociation have an acid reaction; their solutions are colourless. The beryllium silicates of natural occurrence are completely decomposed by fusion with 4 parts of sodium carbonate, and most of them are decomposed by heating them with concentrated sulphuric acid.

Anhydrous *beryllium chloride*, which may be prepared by igniting a mixture of beryllium oxide and carbon in a current of chlorine (or by moderate ignition in carbon tetrachloride vapour, L. Meyer and R. Wilkens) is white, crystalline, sublimable, hygroscopic, and readily soluble in water.

3. *Potassium hydroxide, sodium hydroxide, ammonia, and ammonium*

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[1] *Cf.* p. 162, footnote 1.

[2] The following sections have been largely based (especially Secs. 44 to 55) upon the comprehensive survey of the analytical chemistry of the rare earths by R. J. Meyer and O. Hauser (*Die Chemische Analyse*, XIV.-XV., 1912; Stuttgart, F. Enke), and upon the chapters contributed by R. J. Meyer to Abegg's *Handbuch der anorganischen Chemie*. This reference is all that can be made here to the very thorough treatment of the subject and to the extensive bibliography in both books.

sulphide, precipitate a white flocculent hydroxide from solutions of beryllium salts. When freshly precipitated, this is slightly soluble in ammonia solution and readily soluble in potassium and sodium hydroxide solutions, and can be precipitated from these solutions by means of ammonium chloride (in the altered condition it is insoluble in alkali hydroxide solutions). Concentrated (*i.e.* containing a large amount of alkali hydroxide) alkaline solutions remain clear on boiling, but in the case of more dilute solutions beryllium hydroxide is precipitated, even on standing for some time, owing to the gradual but extensive hydrolytic dissociation of the beryllium hydroxide in the solution into another modification which is less soluble. After the liquid has been boiled for some time the precipitation is complete. (Distinction from aluminium, but only applicable to complete separation therefrom when pure potassium hydroxide (not sodium hydroxide) is used, and when the dilution is not too great.[1])

Tartaric acid prevents the precipitation by alkali hydroxide. *Baryta water* also precipitates the hydroxide, the precipitate dissolving in excess of the reagent; the solution remains clear on boiling. When boiled for some time with *ammonium chloride* the freshly-precipitated hydroxide is dissolved as beryllium ion, with the liberation of ammonia. (Distinction from aluminium hydroxide.) On heating a 10 per cent. solution of sodium hydrogen carbonate containing a beryllium salt to boiling point there is no precipitation of beryllium hydroxide (a good method of separation from aluminium ion and iron ions, C. Parsons and S. K. Barnes [2]). Methyl-, ethyl-, and dimethylamine precipitate beryllium hydroxide; an excess of the reagent does not redissolve it. (Distinction from aluminium ion, but not from iron ion, Renz.[3])

4. *Alkali carbonates* produce white precipitates, the composition of which varies with the conditions. As a rule a basic carbonate is formed; this, when freshly precipitated, is soluble in a large excess of potassium or sodium carbonate solution, and in a much smaller excess of ammonium carbonate solution. This is a particularly characteristic distinction from aluminium ion, but, owing to the fact that in the presence of beryllium ion a certain amount of aluminium hydroxide is also dissolved by ammonium carbonate solution (Joy), it does not afford a basis for the complete separation of the two ions. On boiling the ammonium carbonate solution the beryllium ion separates readily and completely as basic carbonate, but on boiling the solution produced by potassium or sodium carbonate a portion of the beryllium separates as hydroxide, although only after dilution.

Barium carbonate does not form a precipitate when digested with the solution in the cold, but does so when boiled therewith. According to the detailed investigations of F. Haber and C. v. Oordt,[4] the *solubility* of beryllium hydroxide and carbonate precipitates decreases materially *with the age* of the precipitates. The hydroxide which separates when diluted alkaline solutions are allowed to stand is in the altered form, and is therefore no longer soluble. It may be dissolved, however, by washing it and boiling it with potassium hydroxide solution.

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[1] According to A. Zimmermann the separation is complete when 0·3 grm. of the earths is dissolved in 300 c.c. of dilute potassium hydroxide solution; in the case of more dilute solutions aluminium hydroxide is precipitated simultaneously with the beryllium hydroxide.

[2] *Zeitsch. anal. Chem.*, **46**, 292.

[3] *Ber.*, **36**, 2751.

[4] *Zeitsch. anorgan. Chem.*, **38**, 377.

5. On treating a solution of a beryllium salt with *diammonium hydrogen phosphate* (disodium hydrogen phosphate cannot be used instead) in considerable excess, dissolving the resulting precipitate in hydrochloric acid, heating the liquid and adding ammonia solution, drop by drop, until the reaction is neutral (an excess must be avoided), and then boiling the liquid for some time, the original slimy precipitate (beryllium ammonium phosphate) becomes crystalline and rapidly subsides. Citric acid does not prevent the reaction (Distinction from aluminium ion, which under the same conditions never forms a crystalline precipitate, and in the presence of citric acid gives no precipitate at all.) The presence of much aluminium ion prevents the separation of the precipitate of beryllium ammonium phosphate in presence of citric acid (C. Rossler).

6 *Oxalic acid and oxalates* do not produce a precipitate in concentrated solutions of beryllium salts (distinction from the ions of thorium, zirconium, yttria earths, cerite earths, lanthanum, and didymium), but a concentrated solution of potassium hydrogen oxalate precipitates beryllium potassium oxalate

7. When fused with 2 parts of potassium hydrogen fluoride, KF.HF, beryllium oxide yields a fused mass which is soluble in water acidified with hydrofluoric acid. (Method of separation from aluminium oxide, which when treated in the same way is left as a residue of aluminium potassium fluoride.)

8 *Sodium thiosulphate* does not produce a precipitate in solutions of beryllium salts

9 For the separation of aluminium ion from iron ion Haber and van Oordt[1] recommend a method based on the different solubility of the acetates in chloroform. If the hydroxides are dissolved in glacial acetic acid and the solution diluted with water, concentrated by evaporation and extracted with chloroform, the beryllium acetate is removed by the chloroform, whilst the acetates of aluminium and iron remain in the aqueous layer.

For the separation of aluminium ion from beryllium ion Havens[2] has proposed to treat the solution of the chlorides with equal parts of concentrated *hydrochloric acid* and *ether*, and to saturate the liquid with *gaseous hydrogen chloride*. Aluminium chloride separates as an insoluble deposit, which can be filtered off in a Gooch crucible, whilst beryllium chloride remains in solution.

For the detection of a small amount of beryllium ion in the presence of aluminium ion the hydroxides are dissolved in hydrochloric acid, the solution evaporated to dryness, and the residue dissolved in water, with the addition, if necessary, of a very small quantity of hydrochloric acid. The

[1] *Zeitsch. anorgan. Chem.*, **40**, 465.

[2] *Ibid.*, **13**, 435.

solution is transferred to a tube of resistant glass fused together at the lower end, and treated with potassium sulphate (about 12 parts to 1 part of alumina), and sufficient water to dissolve the salt when heated, and the tube, after its other end has been closed by fusion, is heated at a low temperature until everything is in solution, and then for half an hour at 180° C. After cooling, the tube is opened, the separated basic aluminium sulphate filtered off, the filtrate treated with ammonia, and the resulting precipitate separated and dissolved in hydrochloric acid. To this solution is added sufficient citric acid to prevent any precipitation on the addition of ammonia, and the beryllium ion then precipitated as ammonium beryllium phosphate (*cf.* 5, also Sec. 40, 9) (C. Rossler).

10. *Morin* does not fluoresce with solutions of beryllium salts.

11. When moistened with *cobaltous nitrate solution* and ignited beryllium compounds yield grey masses.

12. For the *microchemical detection* of beryllium, see Haushofer, *Mikroskopische Reaktionen*, p. 23, and Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 47.

SEC. 44.

2. **Thorium**, Th, 232·4.[1]

1. *Thorium* is a tetravalent metal, which has not yet been isolated in an absolutely pure condition; the preparations hitherto obtained contain much oxide, and are of a dark grey colour. Thorium occurs in the presumably identical minerals thorite and orangite in the form of silicate, in thorianite as oxide, and in monazite as phosphate. The specific gravity of the unwrought metal is about 11·0; its melting point about 1700°. It is stable in the air, and radio-active. On gentle heating it ignites and burns with a brilliant flame to thorium dioxide. The metal is readily soluble in hydrochloric acid, with the liberation of hydrogen, dissolves with more difficulty in sulphuric acid and hydrofluoric acid, and is insoluble in nitric acid and in alkali hydroxide solution.

2. The *oxide* (dioxide, thoria), ThO_2, is white, or frequently grey, owing to the presence of even traces of impurities; when ignited it becomes incandescent, the light in the absence of cerium being faintly pale blue, and in the presence of cerium of a light bluish tint. After ignition it is only gradually converted by heating with sulphuric acid into a sulphate which is soluble in ice-water and in dilute sulphuric acid; it is insoluble in other acids, and on fusion with alkalis. On evaporating thoria, obtained by the gentle ignition of the oxalate, with hydrochloric or nitric acid, there is produced a colloidal milky-white solution of thorium dioxide, which by transmitted light appears pure yellow. A similar sol may be obtained from the precipitated hydroxide by treatment with thorium nitrate at the boiling temperature, or by treatment with a small amount of aluminium chloride, ferric chloride, or hydrochloric acid. Colloidal solutions of this kind may also be prepared by long-continued treatment of thorium salts with very pure water, or by dialysis. The

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[1] See p. 173, footnote 2.

addition of an electrolyte precipitates the resulting sol. *Thorium hydroxide*, $Th(OH)_4$, dissolves readily in acids when in the moist condition, but only with difficulty after drying. *Thorium chloride*, $ThCl_4$, sublimes at an incipient white heat. It forms only a few extremely unstable complex salts of a thorium hydrochloric acid, since thorium as the most positive member of its group (periodic system) shows the least tendency to form complexes. Thorite, thorium orthosilicate, is decomposed by moderately concentrated sulphuric acid and by concentrated hydrochloric acid.

3. *Potassium hydroxide*, *ammonia*, and *ammonium sulphide* precipitate from solution of the salts white thorium hydroxide, which is insoluble in excess, even in the case of potassium hydroxide. (Distinction from aluminium and beryllium hydroxides.) Hydroxylamine hydrochloride does not inhibit the precipitation by ammonia and ammonium sulphide (distinction from uranium ion); tartaric acid prevents the precipitation. Aniline precipitates the hydroxide from solutions of thorium salts. (Distinction from the ions of cerium, lanthanum, didymium, and yttria earths, A. Kolb.[1]) The precipitation is promoted by the presence of ammonium salts.

4. *Potassium carbonate* and *ammonium carbonate* precipitate basic thorium carbonate, which dissolves readily in excess of the precipitant when concentrated, and with difficulty when dilute. (Distinction from aluminium ion.) The solubility of thorium salts (including the oxalates and phosphates) in alkali and ammonium carbonate solutions may be utilised in a method of separating thorium ions from the ceria earth ions, which form almost insoluble double salts with alkali carbonates. The ammonium carbonate solution deposits the basic salt again even at 50°. *Barium carbonate* precipitates thorium ion quantitatively even in the cold.

5. *Hydrofluoric acid* gives a precipitate of thorium fluoride which is gelatinous at first, but becomes granular on standing. It is insoluble in water and hydrochloric acid. (Distinction from the ions of aluminium, beryllium, zirconium, and titanium.)

6. *Oxalic acid* and also *ammonium oxalate* produce in neutral and not too strongly acid solutions a white, very fine precipitate. (Distinction from aluminium and beryllium ions.) When this is produced in a boiling slightly acid solution and then allowed to stand for some time in the cold, it becomes coarsely granular, and will not pass readily through a filter paper. This precipitate of thorium oxalate, $[Th(C_2O_4)_2 + 6H_2O]$, is practically insoluble in oxalic acid solution, and only very slightly soluble in dilute mineral acids (distinction from yttrium, cerium, and zirconium ions), but is readily soluble in a solution of ammonium acetate containing free acetic acid. It dissolves fairly readily in boiling concentrated solutions of alkali oxalates, especially ammonium oxalate, with the formation of very stable complex salts with the anions $[Th(C_2O_4)_4]''''$, or $[Th(C_2O_4)_3]''$, or $[Th_2(C_2O_4)_5]''$. On cooling and diluting the solution there is no reprecipitation of thorium oxalate, provided that a sufficient excess of ammonium oxalate is present. (Distinction from the ions of ceria earths, lanthanum, didymium, and to a certain extent from those of the yttria earths, although the oxalates of the latter

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[1] *Journ. prakt. Chem.* (N. F.). **66**, 59.

are not so insoluble in ammonium oxalate solution as those of the three first groups of oxalates.) On the addition of acid, especially hydrochloric acid, the resulting free complex acid, $[Th(C_2O_4)_4]H_4$, is readily decomposed and thorium oxalate is re-precipitated. (Distinction from zirconium oxalate, which is not precipitated under the same conditions.) Thorium oxalate may be separated from the oxalates of the other earths (with the exception of those of the partially dissolved yttria earths) by precipitating them together from an acid solution, and extracting them with saturated ammonium oxalate solution.

7. A concentrated solution of *potassium sulphate* precipitates thorium ion slowly but completely. (Distinction from the ions of aluminium, beryllium, and yttria earths.) The precipitate, potassium thorium sulphate, $K_4Th(SO_4)_4.2H_2O$, is insoluble in a concentrated solution of potassium sulphate, but dissolves slowly in cold and readily in hot water. On the other hand, the corresponding sodium double sulphate is readily soluble even in saturated sodium sulphate solution, in contradistinction to the behaviour of the ceria earth compounds, whilst the yttria earth metals form soluble double salts both with potassium and sodium. Anhydrous neutral thorium sulphate is soluble in ice-water, but on heating the solution even to the ordinary temperature it separates in the hydrated sparingly soluble condition. (Distinction from the ions of aluminium, beryllium, the yttria earths, titanium, zirconium, and of the ceria earths (up to lanthanum), the hydrated sulphates of which dissolve with the most difficulty, after those of thorium.) This behaviour of the thorium ion is very important, and may be used (preferably below 20°) for its quantitative separation from the ions of the other earths. If the salt is reconverted by heating from the hydrated into the anhydrous condition it is again soluble in ice-water. (Distinction from titanate ion. Kruss and Nilson.)

8. If thoria is suspended in *potassium hydroxide solution* and subjected to a current of *chlorine* it does not dissolve. (Distinction from many other earths, but not from cerium oxide, which is converted into ceric hydroxide and remains insoluble. Lawrence Smith.)

9. *Sodium thiosulphate* precipitates from boiling neutral or slightly acid solutions of thorium salts a mixture of *thorium hydroxide* or *basic thiosulphate* with sulphur. (Distinction from the ions of ceria and yttria earths with the exception of scandium.)

10. *Potassium ferrocyanide* produces a white precipitate in neutral and slightly acid solutions (a very sensitive reaction in neutral solution).

11. *Potassium azide* (potassium hydronitrate), KN_3, precipitates *thorium hydroxide* (or *basic thorium azide*) from slightly acid solutions containing thorium ion (distinction from the other trivalent ions of the earth metals of monazite), whilst hydronitric acid escapes:

$$Th^{\cdot\cdot\cdot\cdot} + 4N'_3 + 4H_2O = Th(OH)_4 + 4HN_3$$

$$e.g.\quad Th(NO_3)_4 + 4KN_3 + 4H_2O = Th(OH)_4 + 4HN_3 + 4KNO_3$$

(Dennis and Kortright,[1] Dennis[2]). This is a very characteristic reaction of thorium. According to Curtius and Darapski (*J. prakt. Chem.* (N.F.), **61**, 412, 413), zirconium ion is also quantitatively precipitated, even in the cold, from a neutral solution, and yttrium ion on boiling.

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[1] *Zeitsch. anorgan. Chem.*, **6**, 35; *Zeitsch. anal. Chem.*, **34**, 82.

[2] *Zeitsch. anorgan. Chem.*, **13**, 112; *Zeitsch. anal. Chem.*, **38**, 49.

12. *Iodic acid* produces a crystalline precipitate of *thorium iodate* in a nitric acid solution containing thorium ion. The best method of applying the reaction is to acidify 2 c.c. of the solution under examination with nitric acid (free hydrochloric acid must not be present), and then to add 5 c.c. of a solution of 15 grms. of potassium iodate in 50 c.c. of nitric acid of sp. gr. 1·4 and 100 c.c. of water. The iodates of other earth metals, which are sometimes simultaneously precipitated, are re-dissolved when they are boiled with 10 c.c. of a solution of 4 grms. of potassium iodate in 100 c.c. of dilute nitric acid and 400 c.c. of water, since they are all soluble in nitric acid. The remaining precipitate must not disappear on the further addition of the dilute potassium iodate solution. By this means it is possible to detect thorium ion in a dilution of 1 : 10,000. Zirconium, titanium, and tetravalent cerium behave in a similar manner, but may easily be distinguished, the first two by the reactions in Secs. 45 and 52, and the last by reduction with sulphur dioxide, after which it does not give the reaction.

13. *Hydrogen peroxide* precipitates all the thorium ion in the form of a white gelatinous precipitate of *thorium peroxide hydrate*, especially on heating, from neutral solutions, or those slightly acidified with sulphuric acid, or from solutions containing excess of ammonium carbonate. (Distinction from the ceria earths; in the presence of the latter, however, the precipitate invariably contains cerium.) The precipitate is soluble in presence of a large amount of sulphuric acid (Cleve,[1] Wyrouboff and Verneuil,[2] Pissarjewski[3])

14. A concentrated solution of *sodium hypophosphate*, $NaHPO_3 + 2H_2O$,[4] produces in boiling solutions of thorium salts in strong hydrochloric acid a flocculent precipitate of thorium hypophosphate. (Distinction from the ions of the trivalent earth metals.) Titanic acid, ceric ion, and zirconium ion yield appreciable precipitates, but any cerium still present may be reduced by a preliminary boiling, and the titanic acid converted by the addition of hydrogen peroxide into yellow pertitanic acid, which does not give the reaction. For the separation of zirconium, which is simultaneously thrown down, the precipitate is heated, with concentrated sulphuric acid with the addition of sodium nitrate, and the resulting solution of orthophosphates in sulphuric acid treated with oxalic acid, which precipitates only the thorium oxalate.

15. A solution of *fumaric acid* in 40 per cent. alcohol precipitates from a solution of a thorium salt (in 40 per cent. alcohol) the whole of the thorium ion in the form of a salt of fumaric acid. (Distinction from the

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[1] *Bull. Soc. Chim.*, **43**, 53.

[2] *Compt. rend.*, **126**, 310.

[3] *Zeitsch. anorgan. Chem.*, **31**, 359.

[4] Prepared as described by Salzer, *Ann. d. Chem.*, **187**, 322, or of Rosenheim and Pinsker, *Ber.*, **43**, 2003.

ions of the other earth metals except zirconium and erbium. Floyd J. Metzger.[1])

16. *Metanitrobenzoic acid* produces a white precipitate in a neutral aqueous solution of a thorium salt. The addition of a few c.c. of an aqueous solution of aniline metanitrobenzoate renders the precipitation complete (A. Kolb and Ahrle[2]). (Distinction from cerous, lanthanum, and didymium ions, but not from ceric ion.)

17. For the *microchemical detection* of thorium, see Haushofer, *Mikroskopische Reaktionen*, p. 127; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 114.

SEC. 45.

3. Zirconium, Zr, 90·6.

1. Zirconium is a tetravalent metal (sp. gr. 6·4) which has not yet been prepared in an absolutely pure condition. It occurs as *zirconium oxide*, ZrO_2, in varying degrees of purity in large deposits in certain places, as silicate in zircon, and in other minerals containing the rest of the rare earths. In the amorphous form it is a black powder; in the crystalline condition it forms steel-grey scales or hard brittle crystals with a metallic lustre. In the crystalline condition it does not burn below white heat, but in the amorphous state it burns below red heat, emitting a bright light and forming zirconium oxide. It is but little attacked by acids, with the exception of *aqua regia* and hydrofluoric acid. It dissolves most readily in hydrofluoric acid even when dilute. Concentrated sulphuric acid converts it rapidly into a sulphate soluble in water.

2. *Zirconium oxide* (zirconia), ZrO_2, is a white powder, which fuses at about 2700°, and begins to volatilise at about 3000°; it is incandescent when ignited. It is insoluble in hydrochloric acid, but after being heated for some time with a mixture of 2 parts of sulphuric acid and 1 part of water dissolves on the addition of water. Soluble zirconium salts are also obtained by fusion with sodium hydrogen sulphate, or with potassium hydrogen fluoride. The *hydroxide* resembles aluminium hydroxide; when precipitated in the cold and still moist it is readily soluble, but when precipitated hot or dried it dissolves with difficulty in hydrochloric acid. In accordance with the weakly electro-positive character of zirconium, the salts undergo pronounced hydrolytic dissociation in aqueous solution. Hence the solutions show an acid reaction. Crystallisation of the solutions invariably yields basic salts, of which the oxychloride, $ZrOCl_2+8H_2O$, is of especial importance for the preparation of pure zirconium. The tendency of zirconium to form complexes is particularly noticeable in the case of the sulphate, which, unlike the other salts (chloride, nitrates, etc.), which behave in the normal manner, forms complex ions, so that in the electrolysis of solutions of zirconium sulphate the whole of the zirconium goes to the anode. The composition of the resulting zirconium sulphuric acids, some of which can be crystallised, is very variable. They have been studied in detail by

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[1] *J. Amer. Chem. Soc.*, **24**, 901.

[2] *Zeitsch. angew. Chem.*, **18**, 92.

Ruer [1] and by Hauser and Herzfeld.[2] The zirconium silicates of natural occurrence can be decomposed by fusion with sodium hydroxide or sodium carbonate. The fusion is effected at a high temperature after intimate admixture of the silicate with 4 parts of the flux On treating the fused mass with water, sodium silicate is dissolved, leaving a sand-like residue of sodium zirconate, which, when washed, is soluble in hydrochloric acid. Zirconium silicate is also decomposed very readily by fusion with potassium hydrogen fluoride, with the formation of potassium silicofluoride and potassium zirconium fluoride, K_2ZrF_6. *Zirconium chloride*, $ZrCl_4$, may be obtained as a solid, white, sublimable substance, soluble in water, by fusing zirconia with carbon and igniting the resulting zirconium carbide in a current of chlorine, or by treating zirconia for a considerable time with carbon tetrachloride at about 450° (Demarçay [3]), or by causing chlorine containing sulphur chloride to act upon zirconia (Matignon and Bourion [4]). Zirconium chloride is soluble in ether; in the presence of even a small amount of water it forms an oxychloride insoluble in water. A method of separating zirconium from iron ions has been based on this property. The solution of the chlorides is evaporated to dryness, the residue taken up with absolute ether, and the solution filtered. Ferric chloride dissolves, whilst zirconium chloride is left undissolved (Matthews, *Chem. Zentralbl.*, 1899 I., 63).

3. *Potassium hydroxide, sodium hydroxide, ammonia,* and *ammonium sulphide* precipitate a white flocculent hydroxide from solutions of zirconium salts, it is insoluble in excess of the precipitant (distinction from aluminium and beryllium ions), it is also insoluble in boiling ammonium chloride solutions (distinction from beryllium ion). Tartaric acid prevents the precipitation by alkalis and alkali sulphide, owing to the formation of a very stable complex acid with the formula $[ZrO(C_4H_4O_6)]H_2$. A basic tartrate first separates from a concentrated tartaric acid solution, and on the addition of potassium hydroxide is converted into the potassium salt of the complex acid and dissolves. This behaviour towards tartaric acid may be used as a means of separating zirconium from iron ions, since the latter are precipitated by ammonium sulphide from a tartaric acid solution. The behaviour of the separated zirconium hydroxides varies with the previous treatment; hydroxide precipitated in the cold is readily soluble, whilst that precipitated hot or which has been ignited dissolves with difficulty in dilute acids. Hydroxide which has been treated (digested) with hydrochloric acid can form a colloidal pseudo-solution in cold water.

4. The *carbonates of potassium, sodium, and ammonium* gradually produce a white flocculent precipitate of basic *zirconium carbonate.* It is soluble in a large excess of potassium carbonate, more readily in potassium hydrogen carbonate, and very readily in ammonium carbonate solutions. (Distinction

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[1] *Zeitsch. anorgan. Chem.*, **42**, 87; **46**, 449.

[2] Meyer and Hauser, *Die Analyse der seltenen Erden*, p. 144.

[3] *Compt. rend.*, **104**, 113.

[4] *Ibid.*, **138**, 631; *Chem. Zentralbl.*, 1904, I., 1056.

from aluminium ion.) On boiling these solutions gelatinous hydroxide separates.

5. *Oxalic acid* and *ammonium oxalate* produce a fine crystalline precipitate of *zirconium oxalate* in solutions of the normal salts which contain the zirconium as cation (more slowly when the solution was made with the aid of heat, and not at all in the case of solutions of zirconium sulphate or zirconium sulphuric acid). (Distinction from aluminium and beryllium ion.) The precipitate is soluble in excess of oxalic acid solution, especially on heating, and dissolves in hydrochloric acid and also in excess of ammonium oxalate solution, even in the cold. (Distinction from thorium ion.) The complex compounds formed with oxalic acid or ammonium oxalate are somewhat more stable than the corresponding thorium compounds. Hence, no precipitate is formed on adding acid to a solution produced by means of excess of ammonium oxalate. (Distinction from thorium ion.) Ammonia, on the other hand, precipitates the whole of the zirconium ion as hydroxide from a solution of the oxalate in excess of ammonium oxalate solution.

6. A concentrated solution of *potassium sulphate* rapidly produces a white precipitate of *potassium zirconium sulphate* insoluble in excess of the precipitant. (Distinction from aluminium and beryllium ions.) This compound, when precipitated in the cold, is soluble in a large amount of hydrochloric acid, but when precipitated from a hot solution is almost insoluble in water and hydrochloric acid. (Distinction from thorium and cerium ions.) Sodium sulphate and ammonium sulphate do not produce a precipitate.

7. *Hydrofluoric acid* does not produce a precipitate. (Distinction from the ions of thorium and of the ceria and yttria earths.)

8. *Sodium thiosulphate* precipitates *basic zirconium thiosulphate* or a mixture of hydroxide and sulphur from boiling solutions of zirconium salts. (Distinction from the ions of the ceria and yttria earth metals.) The precipitation takes place on boiling the solution containing only 1 part of the salt in 100 parts of water (this is important in connection with the quantitative separation of cerous ion).

9. *Sulphur dioxide* precipitates zirconium ion as hydroxide from a very slightly acid solution of zirconium chloride (not the sulphate). The precipitate can be readily filtered, and affords a suitable means of separating zirconium from iron ions (Baskerville [1]).

10. A concentrated solution of *hydrogen peroxide* precipitates from solutions of zirconium oxychloride the whole of the zirconium ion in the form of a white voluminous hydrate of a *peroxide* of the approximate composition $Zr(OH)_3O_2H$. The same precipitate is produced by hydrogen peroxide and ammonia from solutions of the sulphate and nitrate. It is insoluble in 1 per cent. sulphuric acid and in dilute acetic acid. It is partially decomposed when boiled with acids (Bailey). (Method of separating zirconium ion from the ions of titanium, niobium, iron, and aluminium, but not from thorium ion.)

11. Zirconium ion is completely precipitated as *zirconium oxyiodate*

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[1] *J. Amer. Chem. Soc.*, **16**, 475; *Chem. Zentralbl.*, 1894, II., 299.

on adding an *alkali iodate* to neutral or slightly acid solutions of a zirconium salt. Heat promotes the precipitation (Th. Davis, jun.). The precipitate is only very sparingly soluble in water, in excess of the precipitating agent, and in acids. (Method of separating zirconium ion from aluminium ion.)

12. If the precipitate of zirconium hydroxide produced by ammonia is separated from the filter and dissolved in hot hydrochloric acid, the solution evaporated nearly to dryness on the water-bath, the residue taken up in a little water, and the solution treated, drop by drop, with concentrated hydrochloric acid in the cold, there is produced an abundant precipitate of *zirconium oxychloride* (zirconyl chloride), $ZrOCl_2 + 8H_2O$. (In the presence of insufficient acid a gelatinous precipitate may easily be obtained.) The precipitate dissolves on heating the liquid, but separates again, on cooling, in the form of silken needles. This is a particularly characteristic reaction for zirconium ion (Ruer [1]).

13. On adding zirconium solution, drop by drop, to a boiling solution of sodium salicylate, *zirconium salicylate* is precipitated. (Distinction from titanium. Dittrich and Freund [2].)

14. *Potassium ferrocyanide* produces in neutral solutions a white, and in acid solutions a greenish-yellow, precipitate of *zirconium ferrocyanide*. (No precipitate, or hardly any, is obtained with solutions of the sulphate.) (Distinction from ions of the yttria earth metals.)

15. When turmeric paper is dipped into solutions of zirconium salts slightly acidified with hydrochloric or sulphuric acid, and then dried, it becomes reddish-brown. (Distinction from the other earths.) If titanic acid is present, which under the same conditions gives a brown coloration to turmeric paper, and so masks the zirconium reaction, the acid solution is first treated with zinc in order to reduce the tetravalent into trivalent titanium, the solution of which does not affect turmeric paper (Pisani).

16. For the *microchemical detection* of zirconium, see Haushofer, *Mikroskopische Reaktionen*, p. 156, and Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 111.

SEC. 46

4. Elements of the Yttria Earths.

Scandium, Sc, 44·1; **Yttrium**, Y, 89·0; **Europium**, Eu, 152·0; **Terbium**, Tb, 159·2; **Gadolinium**, Gd, 157·3; **Dysprosium**, Dy, 162·5; **Holmium**, Ho, 163·5; **Erbium**, Er, 167·7; **Thulium** Tu, 168·5; **Ytterbium**, Yb, 173·5; **Lutetium**, Lu, 175·0

The trivalent elements, grouped together under the collective name of "Yttria earths," occur as silicates in the minerals gadolinite (ytterite) and rowlandite, as phosphates in xenotime, as niobates in fergusonite, and as niobates and tantalates in euxenite, yttrotantalite, and some other rare minerals. In the case of the minerals mentioned they usually occur in greater preponderance than the other rare earths also invariably present;[1] since they differ chemically from the latter much more than they do from one another, the original classification, based upon their occurrence in common, of all the characteristic rare earths into yttria and ceria earths has been retained and is in general use. In the yttria earth group yttrium is always present in the greatest proportion, erbium coming next. Scandium is also relatively widely distributed, and has recently been found in numerous minerals, notably in wolframite and tin ores. The rest of the yttria earths are all exceedingly rare, dysprosium being the least uncommon. Owing to their rarity and the great difficulty of preparing them in a pure condition the individuality of the above-mentioned elements has not yet been determined beyond doubt. Whilst the separation of ceria and yttria earths can only be effected by frequently repeated fractional precipitation or crystallisation, *i.e.* by processes of a more preliminary nature, the separation of the individual yttria earths from each other is quite impossible by the ordinary analytical methods. Although in their occurrence and chemical properties certain gradational relationships corresponding to the atomic weights exist between them, so that a distinction can be drawn between the sub-groups of the terbium earths (Eu, Gd, Tb), the erbium earths (Dy, Er, Ho, Tu) and ytterbium earths (Yb, Lu), it is not possible, within the limits of this book, to deal more fully with the slight gradational differences between the different elements, or to describe the analytical behaviour of each individual. We must, therefore, restrict ourselves to giving an outline of the behaviour of yttrium, and to calling attention to the places where the other yttria earths cause deviation from the ordinary analytical course.

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[1] *Zeitsch. anorgan. Chem.*, **46**, 456.

[2] *Ibid.*, **56**, 344.

1. *Yttrium*, Y, like the other yttria earth metals, has not yet been prepared in a pure condition. In the impure state it is a grey powder, which can be polished, has a very high melting point, and burns with a brilliant flame to oxide. It may be prepared by the electrolysis of fused sodium yttrium chloride, or by the reduction of yttria with magnesium.

2. *Yttrium oxide*, Y_2O_3, is white in the pure condition, but yellow when mixed with the other yttria earths. The colour of the oxides and salts is an important characteristic for the differentiation of the individual earths, so that a distinction is drawn between coloured and colourless earths. Thus erbium oxide is pink, and its salts in solution are also deep pink, whilst those of europium are faint pink, those of holmium distinctly pink, and those of dysprosium and thulium are light green or bluish-green. The oxides and salts of the rest of the yttria earths are colourless. When ignited in a Bunsen flame yttrium oxide emits a bright white light, and erbium oxide a strong greenish light. The oxides are crystalline at high temperature, and are appreciably volatile at the temperature of the arc-light; they are almost insoluble in water, but all dissolve in dilute acids, rapidly or slowly according to the previous treatment. The yttria earths

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[1] Some details as to the methods of decomposing the minerals are given on p. 188. (Elements of the ceria earths, 1.)

are all bases of medium strength, and in this respect may be placed between the alkaline earth oxides and alumina. Yttrium is the most positive, and the others, so far as has been determined, then come in the following order : . . gadolinium, terbium, erbium, ytterbium, . . . scandium. The gradation in the case of yttrium to scandium, in accordance with their separate position in the periodic system, is much greater than that between the other elements ; hence, scandium shows a far closer resemblance in its reactions with beryllium on the one hand and thorium on the other than do the remainder of the group. The individual earth metals separate in the order given above when fractionally precipitated with bases, or on decomposition of their nitrates by fusion, so that the most strongly basic yttrium is always precipitated or decomposed last. Its separation from the others is relatively easy, owing to the fact that it becomes concentrated in the last fractions. Only in the case of terbium is a higher oxide (Tb_4O_7) known with certainty ; it is black and, owing to its exceedingly intense colouring power, produces the characteristic yellow coloration of the terbium earths, even when present in only a minute quantity.

3. The *salts*, with the exception of those of scandium, only undergo slight or very slight hydrolytic dissociation in aqueous solution ; the yttria earths form neutral salts even with weak acids. The tendency to form complex salts is much smaller than in the case of thorium and zirconium, but greater than in that of the ceria earths. The greater solubility of the double sulphates is of especial importance for the separation of the yttria earths from the ceria earths. The chlorides crystallise with $6H_2O$; at 120° they are converted into insoluble oxychlorides, $YOCl$; they may be distinguished from the chlorides of the ceria earth metals by their much greater solubility in pyridine (doubtless with the formation of double compounds). The anhydrous chlorides (YCl_3) are only very slightly volatile, yttrium chloride and scandium chloride being the most volatile. (Distinction from aluminium, beryllium, and zirconium chlorides.)

4. *Ammonia*, *sodium hydroxide*, *potassium hydroxide*, and *ammonium sulphide* precipitate a white hydroxide insoluble in excess of the precipitant. (Distinction from aluminium and beryllium ions.) The addition of tartaric acid, citric acid, and other hydroxyl acids, prevents the precipitation of hydroxide, but ammonia produces a white flocculent precipitate of an ammonium double tartrate in tartaric acid solutions, even in the cold. Potassium hydroxide produces a corresponding precipitate in boiling tartaric acid solutions. (Characteristic distinction from the ions of aluminium, beryllium, zirconium, thorium, the ceria earth metals, and, according to some authorities (v. Panayeff), also from erbium ion.) Sodium hydroxide, however, does not produce a precipitate even in the case of the yttria earth metals. The hydroxides precipitated from hot solutions are gelatinous and can be easily filtered, whilst those precipitated in the cold are slimy and difficult to wash ; the hydroxides of yttrium and erbium attract carbon dioxide readily from the air.

5. *Alkali carbonates* give a precipitate of white yttrium carbonate, the carbonates of the "coloured" earths being correspondingly coloured ; the

less positive members also form basic carbonates. The precipitated carbonates re-dissolve on the addition of an excess of alkali carbonate, double carbonates being formed in the process. Double carbonates containing water of crystallisation crystallise after standing for some time from concentrated solutions, especially in the case of yttrium, but not in that of erbium, but their solubility is considerably greater than that of the corresponding ceria earth carbonates, from which they can be quantitatively separated by dissolving them together in concentrated potassium carbonate solution and diluting the liquid with water, which causes the ceria earth carbonates to precipitate. Yttrium carbonate is more soluble in potassium hydrogen carbonate and ammonium carbonate solutions than in potassium carbonate solution (but not nearly so soluble as the corresponding beryllium precipitate). The ammonium carbonate solution of the pure hydroxide deposits all the yttria on boiling, but if ammonium chloride is also present it is decomposed, on further heating, with the liberation of ammonia, and the yttria is re-dissolved as yttrium ion.

6. *Oxalic acid* and *ammonium oxalate* produce at first an amorphous, caseous precipitate, which rapidly becomes crystalline, especially on heating, it has the general composition $R_2(C_2O_4)_3$, with, as a rule, $10H_2O$. The precipitate is almost insoluble in water and oxalic acid solution, dissolves with difficulty in mineral acids, and with great difficulty in excess of oxalic acid solution. (*Most important distinction of the whole group of rare earth ions* (with the exception of zirconium ion) *from aluminium ion, beryllium ion*, etc.) In the case of the rare earths the solubility of the oxalates of the yttria earths is, as a rule, greater than that of the ceria earth oxalates ; also when boiled with concentrated *alkali oxalate* solution the yttria earth oxalates, especially scandium oxalate, dissolve more readily, forming double oxalates, but on diluting and cooling the solution there is usually complete precipitation. (Distinction from thorium ion.)

7. *Potassium sulphate* does not form a precipitate, since yttrium potassium sulphate is readily soluble in water and in potassium sulphate solution. (Distinction from the ions of thorium, zirconium, and the ceria earth metals.) As regards the group of yttria earths, the double sulphates of the terbia earth metals are, with the exception of the very sparingly soluble scandium double sulphates, the least soluble ; they occupy an intermediate position between the ceria earths and the other yttria earths. When fractional crystallisation is used for the complete separation of the latter, the terbium double sulphates remain, for the most part, with those of the ceria earths.

8. *Sodium thiosulphate* does *not* form a precipitate, except in the case of scandium. (Distinction from aluminium, thorium, and titanate ions.)

9. *Hydrofluoric acid* precipitates fluorides. (Distinction from aluminium, beryllium, zirconium, and titanate ions.) The precipitate is gelatinous, insoluble in water and hydrofluoric acid ; before ignition it is soluble in mineral acids, the scandium precipitate being also very sparingly soluble in concentrated hydrochloric acid, but after ignition it is only decomposed by concentrated sulphuric acid. Scandium fluoride (like zirconium

fluoride) forms readily soluble double salts. (Distinction from the rest of the rare earth fluorides.)

10. *Hydrogen peroxide* produces in alkaline solutions gelatinous very unstable precipitates of perhydroxides of the general formula $R(O\,OH)(OH)_2$. (Distinction from thorium and zirconium ions, which are also precipitated from neutral and slightly acid solutions.)

11. *Barium carbonate* does not form a precipitate in the cold, and only an incomplete one on boiling. (Distinction from the ions of aluminium, thorium, cerium, lanthanum, and didymium.)

12. *Turmeric* is not changed in colour by acidified solutions of the salts. (Distinction from zirconium ion.)

13. *Iodic acid* does not produce a precipitate insoluble in nitric acid. (Distinction from thorium ion.)

14 *Sodium subphosphate* does not form a precipitate in strong hydrochloric acid solutions. (Important distinction from thorium ion)

15 The *spectroscopic behaviour* of the yttria earths is particularly important Spectroscopic analysis affords the only means of controlling the progress of fractional separation, and of drawing trustworthy conclusions as to the presence or absence of certain elements. The " coloured " earths have very full and absolutely characteristic absorption spectra, of which only the maxima of the especially characteristic bands in the visible part of the spectra of erbium and dysprosium are given here These are 653, 523, 487, 450, and 442μμ for erbium, and 753, 475, 451·5, and 427·5μμ for dysprosium. Solutions of yttrium salts show no absorption bands.

No description can be given here of the distinctive lines at the extreme end of the arc-light spectra, which are very numerous and characteristic in the case of most of the elements in question. Full details will be found in the work of Meyer and Hauser, as also in the text-books mentioned above (p 99)

16 When heated with *borax* or *phosphate* either in the inner or outer flame the yttrium earth compounds yield beads which are clear and colourless both while hot and cold. (Distinction from cerium and didymium.)

17 For the *microchemical detection* of the yttria earths, see Haushofer, *Mikroskopische Reaktionen*, p 148; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 122 (also *Rec. trav. chim. Pays Bas*, **23**, 413; *Chem. Zentralbl.*, 1905, I , 659, where the author describes the behaviour of the yttrium salts of organic acids) Pozzi-Escot and H. C. Couquet (*Compt. rend.*, **130**, 1136; *Chem. Zentralbl.*, 1900, I., 1199), recommend precipitation as chromate for the microchemical detection.

SEC. 17.

Elements of the Ceria Earths.

Lanthanum, La, 139·0; **Cerium,** Ce, 140·25; **Praseodymium,** Pr, 140·9; **Neodymium,** Md., 144·3; **Samarium,** Sa, 150·4.

With the exception of tri- and tetravalent cerium, all the trivalent elements in the group of the ceria earths occur (unlike the yttria earths) only in very small quantities in the minerals mentioned in the preceding sections, but, on the other hand, they are present in preponderating amount (as compared with the yttria earths) as silicates in cerite and orthite, as phosphates in monazite, as niobates and tantalates in æschynite, and as fluorides in fluocerite, as also in a series of still rarer minerals of similar composition. The most common and most important element is cerium; the other members of the group are also not so rare, and are therefore better known than the majority of the yttria earths. We, therefore, describe their reactions separately in the following pages, and here make only a few general introductory observations.

1. The *decomposition* of all the minerals containing the rare earths is effected most certainly by treatment with concentrated, nearly boiling sulphuric acid. The silicate minerals (cerite, orthite, gadolinite), however, like other silicates, can be more simply decomposed by repeated evaporation to dryness with concentrated hydrochloric acid. Phosphates (monazite, xenotime, etc.), the decomposition of which cannot be effected by means of hydrochloric acid, are decomposed with concentrated sulphuric acid, the excess of which is finally evaporated, and the still moist mass is gradually introduced into ice-water and dissolved.

The *niobates*, *tantalates*, and *titanates* (fergusonite, euxenite, æschynite, etc.), are best decomposed by fusing them at a red-heat for a considerable time in the finely powdered condition with five to six times their quantity of *sodium bisulphate*, the mass being cooled from time to time and treated with a few drops of concentrated sulphuric acid to replace that which has escaped. On extracting the fused mass with water niobic acid and tantalic acid separate.

Hydrofluoric acid is also a very suitable disintegrating agent, since it effects the decomposition of the minerals in question (with the exception of niobite and tantalite) without the aid of external heat, in which process the earth acids are dissolved, whilst the earth metals are left as insoluble fluorides.

2. *Metals*. These can be prepared by electrolysis of the fused chlorides or fluorides– they are white or of a slightly yellowish colour, and are fairly stable in the air. Their specific gravity ranges from 6·15 (lanthanum) to 7·7 (samarium), that of cerium being 7·04 They have the following melting points: Cerium, 623°; lanthanum, 810°; neodymium, 840°; praseodymium, 940°; and samarium about 1300° to 1400°. They are good reducing agents; the metallic mixture obtained by electrolysis is therefore frequently used for reductions instead of metallic magnesium; metallic cerium produces abundant sparks when struck with steel; all the metals burn, emitting a brilliant light. They decompose water, with the evolution of hydrogen, and are readily soluble in acids. They form hydrides, nitrides, and carbides.

3. *Oxides*. The natural mixture of ceria earths as obtained, *e.g.* by ignition of the oxalates, is of a brownish-red colour, and presumably consists of a salt-like compound of the rest of the oxides with ceric oxide acting as an acid. The oxides only become crystalline at high temperatures; at

very high temperatures (arc light) they are somewhat volatile. The mixture is soluble in acids, even after ignition, provided that it does not contain more than 40 to 50 per cent. of ceric oxide. As a rule, the solution in acids takes place more rapidly than in the case of the yttria earths, but here, too, the nature of the previous treatment is a decisive factor. The ceria earths are strong bases, and liberate ammonia from ammonium salts, even in the cold. Lanthanum is approximately equal to calcium in basicity, and the other members of the group follow in this order: Trivalent cerium, praseodymium, neodymium, and samarium. Tetravalent cerium has an amphoteric character, and as regards its basicity comes between zirconium and thorium, in accordance with its position in the system.

4 *Salts.* With the exception of the ceric salts, these undergo little, if any, hydrolytic dissociation; the normal carbonates and the salts of other weak acids may be easily prepared. The colours of the salts, which are often characteristic, are given in the description of the individual reactions. There is no pronounced tendency to form complex salts.

The chlorides crystallise with $6H_2O$, with the exception of praseodymium chloride, which has $7H_2O$. When heated to 120° they form insoluble oxychlorides ($ROCl$). They show only a slight tendency towards the formation of double salts, with the exception of the easily prepared double chlorides with certain heavy metals (Pt, Au, Bi, Sb, Sn). The almost non-volatile anhydrous chloride may be prepared by dehydration in a current of hydrogen chloride, by heating the oxides in a current of chlorine containing sulphur chloride, or by treatment with carbon tetrachloride, or phosgene vapour, $COCl_2$. Their melting points decrease, whilst their specific gravities increase from lanthanum to samarium The *double nitrates* of the ceria earth metals with mono- and divalent metals, *unlike* those of the yttria earth metals, can be crystallised from water without decomposition at the ordinary temperature, and are frequently used for fractional crystallisations from nitric acid or neutral solutions. The ammonium double nitrates, $R(NO_3)_3 . 2(NH_4)NO_3 . 4H_2O$ form large tablets; like the magnesium double nitrates $2R(NO_3)_3 . 3Mg(NO_3)_2 . 24H_2O$, and the manganese double nitrates, they are used for the separation of the metals. The stability and insolubility of these salts decreases in the order of the basicity from lanthanum to samarium. The simple nitrates (which always contain $6H_2O$), unlike the corresponding nitrates of the yttria earth metals, decompose when heated into basic nitrates insoluble in water. On further heating more strongly basic insoluble salts, and ultimately the oxides, are obtained, which is also the case with the yttria earth compounds The temperatures of decomposition vary in accordance with the basicity, so that the lanthanum compounds are the most stable

The behaviour of the *sulphates* is especially important and characteristic. On treating ceria earth metals or their hydroxides, carbonates, etc, with sulphuric acid, the solutions yield crystals of sparingly soluble sulphates with water of crystallisation depending on the temperature (usually 12, 8, or $4H_2O$). The sulphates freed from water of crystallisation by heating at 400° to 500° form strongly supersaturated solutions in ice-water, which when heated yield crystals of the salts containing water of crystallisation, the solubility of which decreases with the increase of temperature. These characteristics of the sulphates are made use of both for the separation of the whole group of the ceria and yttria earth metals (which in this respect behave in a very similar manner) from other elements, and also for the separation of the individual earths from one another; a difficulty in connection with the process is the great tendency towards the formation of supersaturated solutions and meta-stable phases. On heating the sulphates to about 1000° C. basic sulphates are formed, and these can be decomposed into oxides by ignition, which in the case of those members of the group which decompose with most difficulty and are most strongly basic require long exposure to a white heat. The very slight solubility of the alkali double sulphates in concentrated alkali sulphate solution is also of importance for the separation of the yttria earths. The sulphates and double sulphates are soluble in a concentrated solution of ammonium acetate; when boiled with a concentrated solution of sodium hydroxide or of oxalic acid they yield the hydroxides or oxalates respectively.

The *carbonates* form double carbonates, which are only very sparingly soluble in concentrated alkali carbonate solution. They are, however, much more soluble in potassium carbonate solution than in sodium or ammonium carbonate solutions, and on the addition of water to their solutions are precipitated in the following order: lanthanum, praseodymium, cerium, neodymium. (Distinction from the yttria earth metals, the double carbonates of which are more soluble)

The *oxalates* are practically insoluble in oxalic acid solution; in mineral acids they are slightly soluble to an extent increasing with their basicity (*Most important distinction for the whole group of rare earths, with the exception of zirconium, from aluminium, beryllium, etc.*) With alkali oxalates they form double oxalates, which are somewhat soluble on heating, but are completely precipitated in the cold. (Distinction from thorium.)

For the *microchemical detection* of the different ceria earth metals, see Haushofer, *Mikroskopische Reaktionen*, p. 40, and Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., pp 128, 130; Pozzi-Escot and H. E. Couquet, *Compt. rend.*, 130, 1136; *Chem. Zentralbl*, 1900, I, 1199.

SEC 48.

5. Cerium, Ce, 140·25.

1. *Cerium* is the only element of the rare earths which is not only trivalent, but also occurs in the tetravalent condition. Hence it forms two series of compounds, cerous compounds derived from cerous oxide, which can only be prepared by reducing ceric oxide with metallic calcium, and ceric compounds, which correspond to ceric oxide, CeO_2. The oxide obtained by igniting the latter or ceric carbonate or oxalate in a current of hydrogen has a composition corresponding to the formula Ce_4O_7; it rapidly absorbs oxygen on exposure to the air, and is converted into ceric

oxide, with the evolution of heat. The cerous salts are white or colourless, and some are soluble in water. The solutions are colourless, have a sweet taste, and *show no absorption spectrum* (see 12).

2. *Potassium* and *sodium hydroxide* and also *ammonia* produce in solutions of cerous salts a white, gelatinous precipitate of *cerous hydroxide*, which, when exposed to the air, absorbs oxygen and becomes first reddish-violet and then pure yellow. It does not dissolve in excess of the precipitant. (Distinction from aluminium and beryllium ion.) Tartaric and other hydroxylated acids inhibit the precipitation owing to the formation of soluble complexes. (Distinction from the ions of the yttria earth metals.)

3. *Alkali carbonate* and *ammonium carbonate* precipitate white cerous carbonate, which is at first amorphous, but gradually becomes crystalline; the double salts formed in concentrated solutions of the precipitant are only very sparingly soluble; they are most soluble in potassium carbonate solution. Barium carbonate is only very slowly precipitated, if at all, in the cold, but is completely precipitated from hot solutions.

4. *Oxalic acid* precipitates white *cerous oxalate*, which is amorphous at first, but gradually becomes crystalline. The precipitation is complete, even from moderately acid solutions. (Distinction from aluminium and beryllium ions.) The precipitate does not dissolve in oxalic acid solution (distinction from zirconium ion), but is soluble in a very large excess of hydrochloric acid and to some extent in a boiling concentrated solution of ammonium oxalate, although it separates again almost completely on diluting and cooling the solution. (Distinction from thorium ion.)

5. A saturated solution of *potassium sulphate* produces, even in somewhat acid solutions, a precipitate of *cerous potassium sulphate* (distinction from aluminium and beryllium ions), which dissolves with difficulty in cold water, more readily in hot water (Bahr), and is practically insoluble in a saturated solution of potassium sulphate. (Distinction from yttrium ion.) The precipitate dissolves when boiled with a large amount of water acidified with hydrochloric acid

6. *Sodium thiosulphate* does not produce a precipitate in boiling solutions of cerous salts, even when very concentrated. The precipitated sulphur carries down only minute quantities of the salt.

7. *Hydrofluoric acid* produces a white precipitate of *cerous fluoride* which is slimy at first; it is insoluble in excess of the precipitant.

8. *Oxidising agents* convert cerous compounds into the corresponding *ceric compounds* the reactions are characteristic, since they distinguish cerium from all the other rare earths, and are associated with easily recognisable changes of colour, which are of especial importance for the detection of the ion.

(*a*) *Persulphates*, *potassium permanganate*, *alkali hypochlorites*, *chlorine*, and *bromine* in *alkaline* solutions gradually convert the cerous hydroxide first precipitated into *yellow ceric hydroxide*, whilst *reddish-violet cero-ceric hydroxides* are formed as intermediate stages; *atmospheric oxygen* acts in the same way, but more slowly (see 2).

Hydrogen peroxide added to a cold *neutral* or *acid* solution containing ceric ions produces, on the addition of *ammonia*, a reddish-brown precipitate of *cerium perhydroxide*, which, according to Pisserjewski,[1] has the formula: $Ce(O.OH)(OH)_3$. On boiling the liquid ceric hydroxide is produced in a readily soluble form, whilst direct oxidation in a hot solution produces cero-ceric hydroxide, which dissolves with difficulty. In this form the reaction is very sensitive. Minute traces of cerium may also be detected in *mixtures of the earths* by means of this test, if dilute ammonia solution is added, drop by drop, until a slight precipitate of hydroxide remains after shaking; the more weakly basic ceric hydroxide is concentrated in this. Earth metals free from cerium give a bluish precipitate; a large amount of iron makes the reaction very uncertain. The addition of hydrogen peroxide to a cold sodium or magnesium acetate solution containing cerous ions and subsequent boiling produces an analogous effect, a yellow basic ceric acetate being finally formed (R. J. Meyer and Koss).[2] When a solution containing cerous ions is poured into a concentrated solution of *potassium carbonate*, the liquid becomes deep red, slowly on exposure to the air, and more rapidly when shaken or when a current of *air* or *oxygen* is introduced, owing to the formation of a cerium peroxide compound, from which, on boiling the solution, or shaking it with a reducing agent (*e.g* arsenious acid), ceric hydroxide is produced.

(*b*) The $Ce^{\cdot\cdot\cdot\cdot}$ ions are very unstable in acid solutions, which renders the oxidation more difficult. The formation of $Ce^{\cdot\cdot\cdot\cdot}$ ions can always be recognised by the solution becoming yellow; such coloration is also produced at first on the addition of hydrogen peroxide, but disappears again, owing to the reciprocal reducing action of the resulting ceric ions and the hydrogen peroxide upon each other.

Potassium and ammonium persulphate effect complete oxidation in sulphuric acid solution, provided that the solution is not so acid that hydrogen peroxide is produced, since in acid solution this has a reducing action; chlorides also have a disturbing influence, since they reduce ceric compounds, with the liberation of chlorine.

On evaporating solutions of cerous salts with *nitric acid* partial oxidation takes place with the production of a yellow coloration. If the resulting ceric ions are eliminated by the addition of alkali nitrate, whereby complex compounds of the type $R_2Ce(NO_3)_6$ are produced, or by the addition of such anions (*e.g.* iodic acid) as lead to the formation of sparingly soluble salts, the oxidation can be made fairly far-reaching.

Gibbs' reaction, which was formerly frequently used, is also based upon oxidation in nitric acid solution. When a cerous salt is dissolved in nitric acid, and the solution diluted with an equal volume of water and boiled for some minutes with a small amount of *lead peroxide*, the liquid becomes yellow, even in the presence of a minute quantity of cerous ion, owing to the formation of ceric salt. On evaporating this solution to dryness and heating the residue until a portion of the acid is removed, no cerium will then be dissolved by water acidified by nitric acid (although any didymium and lanthanum present will be dissolved). An analogous result is obtained by adding *bismuth tetroxide* to the nitric acid solution, complete oxidation being effected even in the cold. Neither reaction, however, is so sensitive as that produced by hydrogen peroxide in ammoniacal solution.

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[1] *Zeitsch. anorgan. Chem.*, **31**, 359; *Chem. Zentralbl.*, 1900, II., 756.

[2] *Ber.*, **35**, 672.

On fusion with *potassium hydrogen sulphate* the cerous salts yield a yellow to yellowish-red mass (Characteristic and sensitive reaction.)

9. On adding potassium or sodium hydroxide to a solution of a cerous salt until the reaction is distinctly alkaline (if much free acid is present it must be evaporated before the addition), evaporating the liquid to dryness, and treating the residue with a solution of *strychnine* in *concentrated sulphuric acid* (about 1 : 1000), a liquid of a bright bluish-violet colour, soon changing to red, is obtained (Plugge).

10 *Ceric oxide, cerium dioxide*, CeO_2, is always produced on igniting *cerous* hydroxide, oxalate, sulphate, nitrate, or carbonate, or *ceric* hydroxide, nitrate or sulphate, or by combustion of the metal. When hot it is lemon-yellow, but when cold is white to pale yellow, according to the previous treatment. Contamination with the smallest amount of praseodymium produces a flesh-coloured to brownish red coloration, probably owing to the presence of praseodymium peroxide Other slight impurities also produce striking alterations in the colour, which are doubtless due to the formation of salt like compounds in which the ceric oxide acts as acid. (Ceric oxide in admixture with the other earths acts as a conveyor of oxygen, and causes peroxide to be formed on ignition, which would otherwise not be produced.) It is *insoluble in acids*, but by treatment with sulphuric acid or fusion with potassium or sodium hydrogen sulphate is converted into ceric sulphate, which is soluble in water. *It dissolves in boiling acids in presence of reducing agents*, *e g.* in nitric acid, on the addition of hydrogen peroxide, or in hydriodic or hydrochloric acids in the presence of alkali iodide or stannous chloride, with the formation of the corresponding cerous compounds, an analogous result is obtained when it is boiled with an excess of acid to which an equal quantity of hydroquinone has been added.

Ceric hydroxide is obtained as a yellow, slimy precipitate by adding alkali hydroxide or ammonia to solutions of ceric salts; when freshly precipitated and dried at 120° it dissolves in nitric acid, forming a red solution It is soluble in hydrochloric acid, with the evolution of chlorine and formation of cerous chloride, and in sulphuric acid, with the formation of a mixture of cerous and ceric sulphates.

Owing to the great tendency of the ion $Ce^{\cdot\cdot\cdot\cdot}$ to be converted into the trivalent condition the yellowish-red *salts* are exceedingly unstable, and, in aqueous solution, undergo strong hydrolytic dissociation. *Ceric chloride* is only known in hydrochloric acid solution, which is easily decomposed with the liberation of chlorine. Ceric sulphate is fairly stable when anhydrous or in the solid condition with $4H_2O$, but in sulphuric acid solution it is decomposed with the evolution of oxygen and formation of cerous ions. The equilibrium between cerous and ceric ions in these solutions, and consequently the composition of the cero-ceric sulphate complexes, which crystallise from the solutions simultaneously with the ceric sulphate, depends upon the temperature and the proportion of sulphuric acid. The lustrous red *ceric alkali double nitrates*, which are readily soluble in water and alcohol, are considerably more stable. The ammonium double nitrate $Ce(NH_4)_2(NO_3)_6$, which dissolves with difficulty in concentrated nitric acid, is of importance for the separation of cerium from the rest of the ceria earth metals, the double nitrates of which are readily soluble in nitric acid.

Owing to progressive hydrolysis the colour of ceric salt solutions gradually fades; freshly prepared solutions become darker again on the addition of acid, owing to the repression of the hydrolysis, but this only occurs to a slight extent in the case of older solutions or those hydrolysed by boiling. When slightly acid solutions, preferably sulphuric acid solutions of ceric nitrate or sulphate, are greatly diluted and boiled *basic salts* separate. This process frequently repeated may be used for the complete separation of cerium from the other earth metal ions.

Reducing agents always decolorise the yellow solutions of ceric salts, with the formation of the corresponding cerous salts. *Hydrogen peroxide* is the most suitable reagent, but the others mentioned above, and also oxalic acid, may be used.

11. *Borax* and *alkali phosphate* dissolve cerium compounds in the outer flame, forming reddish yellow beads (distinction from the earth metals previously described); the colour fades and often almost disappears on cooling. Colourless beads are obtained in the inner flame.

12. *Cerous salts* do not show an absorption spectrum in the visible part of the spectrum (most simple and decisive test of purity; in the case of impure salts absorption lines can be seen, especially in the yellow and green parts of the spectrum). *Ceric salts* darken the blue and violet parts of the spectrum. The *emission spectrum* of cerium is characterised by the presence of exceptionally numerous lines (*cf.* Meyer and Hauser, pp. 85 and 86).

SEC. 49

6. Lanthanum, La, 139.0.

1. *Lanthanum* is a trivalent metal which rapidly turns blue in the air. It is the most strongly basic element of all the rare earth metals.

2. *Lanthanum oxide*, La_2O_3, is white,[1] and does not change when ignited in the air (distinction from cerous oxide); the ignited oxide absorbs carbon dioxide from the air and behaves towards water like calcium oxide, being converted into a milky-white hydroxide, slowly on contact with cold, rapidly with hot water. Both the oxide and hydroxide turn red litmus blue, liberate ammonia from its compounds even in the cold, and dissolve in strong ammonium chloride solution, and also, even after strong ignition, in dilute acids.

3. The *salts* are colourless. Nearly the whole of the lanthanum ion

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[1] Lanthanum oxide is flesh-coloured in the presence of praseodymium; on the other hand, the formation of praseodymium peroxide is prevented by the presence of lanthanum.

separates at 20° to 30° from a saturated solution of lanthanum sulphate in ice-water, as a sulphate crystallising with $9H_2O$, and a method of separation from the ions of the other ceria earths may be based on this property.

4. *Potassium sulphate*, *oxalic acid*, and *ammonium oxalate* (acting upon lanthanum oxalate) and *hydrofluoric acid* give the reactions mentioned in the case of cerous ion.

5. *Potassium hydroxide* produces a slimy, gelatinous precipitate of hydroxide, which is insoluble in excess and does not become brown on exposure to the air. Tartaric acid inhibits the precipitation.

6. The precipitate produced by *ammonium carbonate* is almost insoluble in excess of the precipitant; the lanthanum double carbonate is also more sparingly soluble than the cerous double carbonate in concentrated *potassium carbonate solution*. *Barium carbonate* precipitates lanthanum ion quantitatively from solutions of lanthanum salts, even in the cold.

7 On treating a cold dilute solution of lanthanum acetate with excess of ammonia, repeatedly washing the slimy precipitate, and adding a little powdered *iodine*, a *blue coloration* [1] which gradually permeates the whole mass is obtained. (Characteristic distinction of lanthanum ion from the ions of the other earths, the presence of which, however, frequently has a strong influence upon the reaction)

8 *Sodium thiosulphate* does not precipitate lanthanum from even boiling solutions of the salts.

9 Lanthanum compounds do *not* show an *absorption spectrum*; on the other hand, the violet and ultra-violet *arc spectrum* is rich in characteristic lines.

SEC. 50.

7. **Praseodymium,** Pr, 140·9, and **Neodymium,** Nd, 144·3.

These two very closely similar metals were formerly regarded as one element, *didymium*. They are distinguished from each other by the fact that the neodymium salts are *pink* or *violet*, and show a characteristic pinkish-blue fluorescence, whereas the praseodymium salts are grass-green in colour; the absorption spectra of solutions of their salts are also correspondingly different. Three oxides of praseodymium are known: viz. a yellow *sesquioxide*, Pr_2O_3, from which the salts are derived, the *blackish-brown oxide*, with the probable composition Pr_4O_7 or Pr_6O_{11}, which is produced by ignition of the oxalates, nitrates, etc., and the *black peroxide*, PrO_2, which can be prepared from pure praseodymium salts only by fusion with potassium nitrate; on the other hand, the presence of even small quantities of cerium compounds promotes the formation of peroxide, even when other praseodymium compounds are ignited. The *brown coloration* obtained on igniting the oxides in the presence of cerium compounds is a very sensitive test for praseodymium. On heating the resulting higher oxides at a white heat they are deprived of the whole or part of their oxygen and lose their brown colour. As a rule, however, they regain their oxygen and colour on cooling. Other ceria earths which may be present also appear to have an influence upon the oxides formed—lanthanum, in particular, tends to prevent the formation of peroxides.

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[1] *Cf.* W. Biltz, *Ber.*, **37**, 719.

The only oxide of *neodymium*, however, known with certainty is the sesquioxide, Nd_2O_3. As a rule there is considerably more neodymium than praseodymium in the rare earth minerals. Auer von Welsbach succeeded in separating the two elements by long-continued fractional crystallisation of the double alkali nitrates. It is not possible to effect a separation by means of the ordinary analytical reactions, in which the compounds of both elements completely agree. We shall, therefore, now describe the reactions of their mixture, *didymium*.

1. *Didymium* is trivalent. The *oxide* is grey. Traces of cerium always cause the colour to be brownish, but according to R. J. Meyer and Koss[1] the mixtures of oxides rich in praseodymium are also invariably brown. When the oxide is moistened with nitric acid and ignited a dark brown peroxide with the above-mentioned properties of praseodymium peroxide is obtained. On contact with water didymium oxide is slowly converted into hydroxide. It absorbs oxygen rapidly from the air, does not show an alkaline reaction, and dissolves readily in acids and in boiling ammonium chloride solution.

2. The salts soluble in water and their solutions are pink, whilst concentrated solutions are yellow to brownish in colour, since as a rule neodymium predominates in them. Solutions rich in praseodymium are also brownish or colourless when dilute, but green when the praseodymium is in considerable preponderance.

3. *Potassium hydroxide*, *sodium hydroxide*, and *ammonia* precipitate hydroxide, which is insoluble in excess of the precipitant, does not alter in the air, and readily absorbs carbon dioxide from the air. Tartaric and other hydroxy acids do not prevent the precipitation.

4. *Alkali carbonates* and *ammonium carbonates* give a precipitate of red *didymium carbonate*, which is somewhat soluble in excess of alkali carbonate solutions (*vide supra*, Sec. 47, 4). *Barium carbonate* precipitates didymium ions slowly but quantitatively. The solution of neodymium double carbonate in concentrated potassium carbonate solution is blue, and shows an absorption spectrum, which differs from that of the simple neodymium salt solutions.

5. *Oxalic acid* produces a nearly quantitative precipitate. The resulting reddish *didymium oxalate* dissolves with very great difficulty in cold hydrochloric or nitric acid, but is soluble on heating. *In this respect it behaves like cerous oxalate.*

6. The behaviour of solutions of didymium salts towards *sodium sulphate*, *sodium thiosulphate*, and *hydrofluoric acid* is exactly analogous to that of solutions containing cerous or lanthanum ions.

7. The *didymium peroxide* formed on ignition, the composition of which, as mentioned above, depends upon the purity and conditions of formation, is soluble in hydrochloric acid, with the evolution of chlorine and formation

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[1] *Ber.*, 35, 3741.

of didymium chloride, and in oxygenated acids with the evolution of oxygen and formation of the corresponding salts. It thus behaves as a very characteristic peroxide.

8. When fused with *borax* didymium compounds yield a nearly colourless glass both in the reducing and oxidising flames, and only when a large amount is present is a faint amethyst-red coloration produced. ***Alkali** phosphate* yields bluish to amethyst-red beads in the oxidising flame; the colour disappears in the reducing flame. Fused with *sodium carbonate* in the outer flame didymium compounds yield a greyish-white mass. (Distinction from manganese.)

9. The *absorption spectrum* given by solutions of didymium salts is *especially characteristic* of didymium. It shows the following absorption lines expressed in $\mu\mu$: 596 590 (Pr), **578** (Nd), 532 (Nd), **522** (Nd), **520** (Nd), 511 (Nd), 509 (Nd), **481** (Pr), 474 (Nd), **469** (Pr) and (Nd), **444** (Pr), **427** (Nd). The *emission spectrum* corresponds essentially with the absorption spectrum of the solutions.

SEC. 51.

8. Samarium, Sa, 150·4

Samarium is a trivalent metal. It has only recently been obtained in a relatively pure condition. It is the least basic member of the ceria earths, and forms the transition stage to the terbia earths. Its salts are of a topaz-yellow colour Its reactions agree closely with those of the other ceria earths, the main difference upon which its separation from these is based, consisting in its different basicity as mentioned above (Sec. 47, 4). The *absorption spectrum* shows several characteristic bands, the strongest of which have their maxima at 476, 463, 417 and $402\mu\mu$. The absorption spectrum of samarium, however, is considerably weaker than that of didymium, and is easily masked by the latter. A more trustworthy method than the absorption spectrum for detecting and testing the purity of samarium compounds is afforded by the *arc spectrum*, which shows very many lines.

SEC. 52.

9. Titanium, Ti, 48·1

1. Titanium in the amorphous condition is a grey, in other conditions a silvery-white, metal, which even yet has not been prepared in an absolutely pure state. It occurs in its compounds in the di-, tri-, and tetravalent condition, but only the compounds of tetravalent titanium are stable. The specific gravity of amorphous titanium is about 4·5, and the melting point of the metal about 1800–1850°. It is widely distributed in nature, although usually only in small quantities. It is found as *dioxide* in three different forms— rutile, anatase, and brookite also in numerous *titanates*, notably in titanium iron, $FeTiO_3$, and titanite, $CaTiSiO_5$, as well as in small amount

in bauxite, in many clays and silicates, in ironstone, etc. Hence, titanium is sometimes present in pig-iron and blast-furnace slags, in which it may under some conditions occur in the form of small copper-red cubes of the so-called titanium cyanogen nitride, Ti_5CN_4. The decomposition of the minerals is effected by fusion with sodium or potassium carbonate. In this process carbon dioxide escapes and alkali titanate, R_2TiO_3, is formed, and on extracting the fused mass with water a residue of titanic acid containing alkali is left; the addition of acid causes solution or the separation of a purer titanic acid, according to the concentration conditions. The quantitative separation of the titanic acid thus obtained from iron, which is relatively difficult, is best effected by heating the residue, left on extracting the fused mass with water, to about 300° with twice its weight of concentrated sulphuric acid, dissolving the mixture in a little water, adding acetic acid in the proportion of a third to a fourth of the solution, diluting the liquid and boiling it for several hours, meanwhile replacing the evaporated water. Under these conditions titanium dioxide is precipitated in a fairly pure condition, without any admixture of niobic or tantalic acids. Another method is to mix the ores with carbon and fuse the mixture in an electric furnace. Very pure titanium chloride is obtained by heating the resulting carbides in a current of chlorine.[1]

When heated in the air, *titanium* burns with a bright flame, forming titanium dioxide; it combines with nitrogen at 800°, liberating heat, and forming titanium nitride; it is decomposed by water, but not below 100°, and dissolves in hot dilute acids, especially in hydrofluoric acid, to form salts of trivalent titanium.

2. *Titanium dioxide*, TiO_2 (titanic anhydride), usually separates in the form of a white amorphous powder. When gently ignited it is white, on continuing the heating transitorily becomes lemon-yellow, and when very strongly ignited it may become, according to its previous treatment, yellowish-white, or, if ammonium chloride was originally present, brownish (v. d. Pfordten [1]). It melts at about 1560°, and has a specific gravity which ranges (according to the temperature to which it has previously been heated) from 3·9 (600°) to 4·25 (1200°). By ignition in a current of hydrogen a lower oxide is formed; the dark-coloured products hitherto obtained are not individual substances, but vary in composition from Ti_2O_3 to Ti_7O_{12}. More pronounced reduction is effected by means of alkali metals, magnesium, or aluminium.

Titanium dioxide is insoluble in water, and, after ignition, is not attacked by dilute acids, with the exception of hydrofluoric acid, in which it slowly dissolves. When the solution in hydrofluoric acid is heated the tetrafluoride volatilises, but if sulphuric acid is added before evaporation to dryness, titanium dioxide is quantitatively formed, and no titanium fluoride escapes. (Distinction from silicon dioxide.)

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[1] According to Meyer and Hauser (*loc. cit.*); see also the statements in Abegg's *Handbuch*, Vol III., Part II., and the detailed investigations of v. d. Pfordten on the preparation of pure titanium dioxide from rutile, the most important titanium compounds, and the reactions of solutions which contained di-, tri-, and tetravalent titanium. *Ann. d. Chem.*, **234**, 257 *et seq.*, and especially **237**, 201 *et seq.*

On *heating titanium dioxide with concentrated sulphuric acid*, or better, on *fusing it with alkali hydrogen sulphate*, it is converted into sulphate, which dissolves when diluted with water. When the solution in very dilute sulphuric acid is *boiled for a long time, titanic acid is precipitated* as a white powder insoluble in acids (metatitanic acid). Fusion with alkali hydroxides only causes a small amount of titanium to be dissolved when the fused mass is treated with water, whereas fusion with alkali carbonates effects complete decomposition into alkali titanates as described above (in 1). Fusion with *potassium hydrogen fluoride* produces a transparent mass soluble in dilute hydrochloric acid. Heating the dioxide in a current of *carbon tetrachloride, chloroform, or sulphur chloride* (heating with carbon in a current of chlorine was also formerly used) is a very suitable method of decomposition, *titanium trichloride* being formed in the process

Titanium dioxide shows pronounced *amphoteric* behaviour As a *weak acid* it *forms metatitanates*, R_2TiO_3 (orthotitanates, R_4TiO_4, are not known), which may easily be obtained in the product of fusion, but in aqueous solutions undergo hydrolytic dissociation with the separation of titanic acid ($TiO_2\, xH_2O$). As *cation*, tetravalent titanium, which is described more fully below, also forms salts, which very readily undergo hydrolysis.

3. *Salts*. Titanium forms three (or, including the pertitanates, four) series of salts.

(*a*) *Titanous salts*, which correspond to *divalent titanium*, can only be obtained in the absence of air, and have been but little investigated. Potassium thiocyanate and hydrochloric acid produce a brown coloration in solutions of the salts of divalent titanium, and on shaking the liquid with ether the colour is transferred to the latter (v. d Pfordten).

(*b*) *Titanic salts* in which the titanium is *trivalent*. These also undergo oxidation with extreme readiness, and hence compounds with a strong reducing action are produced by dissolving titanium in dilute acids, or by the action of strong reducing agents upon solutions of the corresponding salts of tetravalent titanium, into compounds of which they are usually converted merely by exposure to the air. Their aqueous solutions are of a *violet* colour, but, as in the case of chromic salts, there are also less stable modifications, which give solutions of a *green* colour; in general the reactions are similar to those of the aluminium and ferric ions. Alkalis precipitate a dark hydroxide, owing to there being a considerable tendency to form complex salts, this precipitation does not take place in the presence of tartaric or other organic hydroxy acids. The oxalates, as also other compounds (*e.g.* that with pyrocatechol, *cf.* 8) of trivalent titanium are yellowish-red.

(*c*) *Salts of tetravalent titanium*. Under ordinary conditions these are the only stable salts; they are colourless in aqueous solution, and usually undergo pronounced hydrolytic dissociation; they invariably form complex compounds in their solutions, whilst the amount of the ion $Ti^{\cdot\cdot\cdot\cdot}$ progressively decreases.

Titanium tetrachloride, the method of preparing which has already been described, is a colourless liquid which has a suffocating odour, boils at 136°, and fumes strongly in the air, hydrochloric acid being liberated, and an oxychloride formed; it dissolves in alcohol, forming a solution which remains clear even on the addition of water, but is decomposed by water with the evolution of heat. This hydrolysis leads, according to the conditions, to the formation of titanium hydroxides, which behave in a different manner. If the titanium tetrachloride is dissolved in very cold water, with precautions to prevent the solution becoming hot (or if it is allowed to stand for some time close to water beneath a bell jar, and the resulting solid crystalline mass introduced into water), a clear or slightly opalescent solution is obtained, which shows little, if any, turbidity on boiling, and in which the addition of an electrolyte produces incomplete flocculation (*α*- or orthotitanic acid). If the solution thus obtained is allowed to stand for some time and then boiled, a copious precipitate of another modification of the hydroxide is produced (*β*- or metatitanic acid). When titanium tetrachloride is mixed with concentrated hydrochloric acid a yellow compound is formed, while heat is evolved and vapours of hydrogen chloride escape; this compound dissolves in excess of hydrochloric acid to form a clear, light yellow, non-fuming liquid, in which presumably the complex ions $TiCl''_6$ are present. The fairly stable solution may be diluted to any extent without any separation of titanic acid. Owing to its ready *volatility* titanium tetrachloride is of *importance in analysis*, in this connection it is necessary to take into consideration its tendency to form volatile compounds with other chlorides, such as PCl_3, PCl_5, etc.

The *tetrafluoride* is a white, very hygroscopic powder, boiling at 284°. When dissolved in dilute hydrofluoric acid it forms titanium hydrofluoric acid, the potassium salt of which K_2TiF_6 is sparingly soluble (1 : 177 at 0° and 1 : 78 at 20°), and is of importance for the separation of the acid from the other earth acids.

The *sulphates* show to a pronounced extent the tendency found in the case of all the other salts, to form basic salts. The only really stable salts among these, "titanyl sulphates," belong to the type $(TiO)SO_4$; they undergo varying degrees of hydrolysis in aqueous solution, and yield, according to the conditions, deposits of strongly basic sulphates or of pure hydroxide (possibly too in the case of these precipitates it may only be a question of a hydroxide adsorbing more or less sulphuric acid). Strong dilution and boiling cause metatitanic acid to precipitate.

(*d*) *Pertitanates.* It was formerly commonly assumed that these contained hexavalent titanium. The solutions of the pertitanates, which have not been completely investigated, are of an orange-yellow colour: these compounds, however, are more correctly regarded as those of a titanium peroxide hydrate (*vide infra*, 9).

Reactions of tetravalent titanium.

4. *Ammonia*, *potassium* or *sodium hydroxide*, *ammonium sulphide*, and *barium carbonate* precipitate *titanium hydroxide* (titanic acid), $TiO_2 + xH_2O$

(or $Ti(OH)_4 + xH_2O$), as a voluminous white precipitate (titanic acid gel) from solutions of the salts of tetravalent titanium; tartaric acid inhibits the precipitation. The precipitate is readily soluble in solutions of alkali carbonates, and especially of ammonium carbonate, but it separates again on boiling the solutions for some time. As was mentioned above in connection with the hydrolysis of the chloride, the hydroxide exists in two modifications, which, however, are only the extreme members of a series of hydrates, which are continually changing into one another. If the precipitation is made by adding ammonia, in the cold, to a freshly prepared solution, and the precipitate washed with cold water, α- or orthotitanic acid is produced; it is readily soluble in dilute acids in the cold, and is somewhat soluble in potassium and sodium hydroxide solutions, but separates again on boiling, and when cautiously heated incandesces and forms titanium dioxide. The β- or metatitanic acid, which is much less soluble in acids and insoluble in alkali solutions, is formed, as was mentioned above, by the hydrolysis of aqueous solutions of titanium salts when boiled for some time. This hydrolysis is complete in the case of sulphates, and when substances such as *sodium acetate* or sulphur dioxide, which promote flocculation, are present in the solution, but in the case of chlorides and many other salts is only incomplete.[1] The very pronounced tendency to sol-formation in solutions of the chlorides is shown by the fact that the titanic acid gel precipitated from the solutions will again become colloidal and pass through the filter, if washed with water, without the addition of an electrolyte.

5 *Sodium thiosulphate* gives a quantitative precipitate of titanium hydroxide in boiling acid solutions of titanium salts. (Distinction from the ions of the trivalent rare earth metals. Agreement with the ions of aluminium, zirconium, thorium, scandium, and tetravalent cerium.)

6 *Disodium hydrogen phosphate* and other solutions containing *phosphate ion* produce, even in strong hydrochloric acid solutions of titanium salts, a nearly quantitative precipitate of basic titanium phosphate, the exact composition of which is not known. The precipitation takes place even in the presence of a large excess of formic acid, and on boiling the liquid with a large amount of sodium acetate and acetic acid. Both methods, and especially the latter, effect complete separation of titanium ion from aluminium ion, although only after repeated treatment (Gooch [2]).

7. *Potassium ferrocyanide* produces in acid solutions a *reddish yellow* precipitate, potassium ferricyanide a *yellow*, and extract of gall nuts a *brownish* precipitate, soon changing to *orange-red*.

8. *Dihydroxylmaleic acid* produces in cold aqueous solutions, even when extremely dilute, an intense *reddish-brown* coloration, and in concentrated

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[1] This affords a means of separating titanic acid from aluminium and iron ions. If the latter is present in the form of ferric ion, the precipitated metatitanic acid invariably contains iron. This may be prevented by introducing sulphur dioxide, or adding sodium thiosulphate.

[2] *Chem. Zentralbl.*, 1887, 153.

solutions a *chocolate-brown* precipitate of *titanium dihydroxymaleic acid*, which resists the action of cold concentrated acids, with the exception of hydrofluoric acid, and forms alkali salts (H. J. H. Fenton [1]). *Pyrocatechol* gives a yellowish-red coloration. This is an extremely sensitive reaction. It depends (as does possibly also the reaction with dihydroxymaleic acid) upon the reduction of the titanium ion to the trivalent condition, and the formation of a yellowish-red precipitate (Piccard [2]). The sodium salt of *chromotropic acid* (1·8-dihydroxynaphthalene-2·4-disulphonic acid) produces a blood-red coloration in sulphuric and hydrochloric acids solutions, but not in those containing much nitric acid. (This is a sensitive and trustworthy reaction.) Titanium compounds give *characteristic colorations* with *phenols*, especially *hydroquinone*, and *alkaloids*, especially *morphine* and *brucine* (Levy [3]), but see also Hall and Smith.[4] Jorissen [5] recommends the red coloration which a solution of *salicylic acid* in concentrated sulphuric acid gives with the titanate ion as especially suitable for distinguishing it from the cerous ion (which also gives a yellow coloration with hydrogen peroxide, *vide* 9). He fuses a little of the substance under examination on a platinum wire with potassium hydrogen sulphate, and treats particles of the crushed bead with the solution of salicylic acid in concentrated sulphuric acid. In the presence of titanate ion the solid particles show a red coloration, which gradually spreads into the liquid

9. *Hydrogen peroxide* produces a *yellow coloration* in sulphuric or hydrochloric acid solutions of titanic acid; *reducing agents* such as stannous chloride and zinc dust decolorise the solution again. In the absence of cerium, molybdate, vanadate, or chromate ions, the reaction is very characteristic and very sensitive (It is capable of detecting as little as 0·005 per cent. of TiO_2 with certainty in sulphuric acid solution.) Hydrofluoric acid inhibits, and the presence of much nitrate or acetate ion also influences the reaction; chlorides, bromides, and iodides are also stated to have a disturbing effect (Levy), and obviously substances such as ferric salts, which produce a yellow coloration, affect the sensitiveness of the test The yellow solution still shows all the reactions of hydrogen peroxide, with the exception of the blue coloration with chromate ion. According to the view formerly held the reaction depends upon the formation of pertitanic acid with hexavalent titanium, but a better assumption is that hydroperoxidates of titanium are formed. A yellow compound is precipitated with a composition corresponding to the formula $Ti(O.OH)(OH)_3$ when the solution of titanyl sulphate, to which hydrogen peroxide has been added, is treated with a little ammonia or alkali hydroxide. The addition of a larger amount of alkali hydroxide or ammonia produces pale yellow solutions, which may be assumed to contain alkali pertitanates or salts, which are able to produce the hydroperoxidate, owing to the fact that the acid character of the rest of the hydroxyl groups is greatly intensified by the introduction of the hydrogen peroxide. (Method for the separation o

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[1] *Chem. Zentralbl.*, 1908, II., 497.

[2] *Ber.*, **42**, 4343.

[3] *Zeitsch. anal. Chem.*, **40**, 807.

[4] *Chem. Zentralbl.*, 1905, II., 1163

[5] *Ibid.*, 1904, I., 55.

titanium and iron ion[1]). Since the hydroperoxidates are readily soluble in acids, the addition of hydrogen peroxide causes modifications of titanic acid, which otherwise are only sparingly soluble in sulphuric acid, to dissolve readily in that acid. A yellow coloration is produced when solid titanium compounds are fused with sodium peroxide, the mass dissolved in a sufficient quantity of cold water (no pronounced heating takes place), and the solution acidified with sulphuric acid.

10 *Reducing agents* produce some further characteristic reactions in solutions containing tetravalent titanium, owing to the formation of titanic ion. For example, *metallic tin* or *zinc* produces a *violet* to *blue coloration* in sulphuric or hydrochloric acid solutions of titanic acid; in the reduction of the fluoride a green coloration may be produced, whilst *alkali hydroxides* or *ammonia* precipitate *blue* or *black titanic hydroxide* from the reduced solution. In contradistinction to niobic acid the green coloration is also produced in a solution of the potassium double fluorides slightly acidified with hydrochloric acid. In *very strong* hydrochloric acid solution niobic acid is rapidly reduced (*cf.* p. 210, 5 (*e*)). *Hydrosulphurous acid*, a solution of which is obtained by the action of granulated zinc upon an aqueous solution of sulphur dioxide, or its sodium salt ($Na_2S_2O_4$),[2] also produce a violet or red coloration even in very dilute solutions; the colouring matter is not extracted from these by shaking with ether (R. Fresenius, *Zeitsch. anal. Chem.*, **24**, 410). The reaction proceeds, as shown in the following equation, from left to right in acid solutions, and from right to left in alkaline solutions, and may thus not take place at all in the latter (Brunck [3])

$$2TiCl_4 + Na_2S_2O_4 \rightleftarrows 2TiCl_3 + 2NaCl + 2SO_2$$

Similar reactions, occasionally differing, however, in the colour of the resulting products, are also given by niobium, molybdenum, vanadium, and tungsten compounds (*cf.* the respective sections). The solutions produced by such reductions have themselves very strong reducing powers, *e.g.* bleaching indigo

11. *Alkali phosphate* dissolves titanium dioxide with difficulty in the point of the outer blowpipe flame forming a colourless glass, but it dissolves it freely and easily in that part of the outer flame in front of the inner point. If the transparent bead is again introduced into the point of the outer flame it becomes turbid, if *sufficiently saturated*, and on continuing the heating with the blowpipe, titanium dioxide separates in microscopic crystals in the form of anatase (G. Rose). According to A. Knop the crystals consist of titanium phosphate, but according to G. Wunder they are *rhombohedral crystals* of *sodium titanium phosphate*. When the bead is introduced into a strong reducing flame it appears after some time yellow while hot, red while semi-cold, and violet when cold. The reduction is facilitated by the addition of a little tin. On adding a small amount of ferrous sulphate the

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[1] *Cf.* Faber, *Zeitsch. anal. Chem.*, **46**, 277, where other literature on hexavalent titanium is mentioned.

[2] *Cf.* footnote to heading Sec 102

[3] *Ann. d. Chem.*, **346**, 283.

bead obtained appears blood-red in the reducing flame. In the oxidation area of the Bunsen flame the phosphate bead is coloured either not at all or only a faint yellow tint—when cold it appears colourless or pale violet. In the reduction area the bead is yellow while hot, and on cooling changes successively to yellowish-green, olive-green, faint violet, and violet. The reduced bead shows a much more pronounced coloration than the oxidised bead when cold. The addition of tin promotes the production of the reduction colorations. *Borax* beads are only faintly coloured by considerable quantities of titanium (Lutz, *Zeitsch. anal. Chem.*, **47**, 21).

12. If a substance containing titanium is fused with *sodium carbonate* on a loop of thin platinum wire in the inner flame of a Bunsen burner, *which has been made somewhat luminous*, and heated until all the sodium has volatilised, the copper-red compound *titanium cyanide nitride*, $3Ti_3N_2 + TiC_2N_2$, is formed through the action of the cyanogen in the gas (Ludeking).

13. *For the detection of titanium in minerals* about 0·1 grm. of the finely powdered substance may be fused with 0·2 grm. of *sodium fluoride* and 3 grms. of *sodium hydrogen sulphate*. On treating the fused mass with cold water the titanic acid is obtained in solution and may be detected therein, *e.g.* as described in 9 (A. Noyes). As a rule, in the analysis of silicates, the titanium dioxide is present in the separated silicon dioxide. In such cases the residue may be fused with potassium hydrogen sulphate either directly or after removal of the silicon dioxide by heating it with hydrofluoric and sulphuric acids, the fused mass dissolved in cold water, and the solution tested with *hydrogen peroxide*. Silicates, *e.g.* refractory materials, may also be fused with sodium peroxide in an iron crucible (see 9, conclusion). Knecht [1] has suggested heating the mixture of silicon dioxide and titanium dioxide with a little dilute hydrochloric acid (1 : 1) and zinc foil, and then after some time adding the solution to a hot aqueous solution of about 0·5 grm. of Rochelle salt which has been tinted blue with *indigo solution*. In the presence of titanium the liquid is decolorised. The test is rendered still more sensitive by using a very dilute solution of *methylene blue* instead of the solution of Rochelle salt and indigo. Titanium iron may be decomposed either by fusion with potassium hydrogen sulphate and extracting the fused mass with water, or, as proposed by Hempel,[2] by fusion in a silver crucible with 4 parts of sodium peroxide. When the mass is extracted with hot water the *residue* will contain all the titanium dioxide together with ferric oxide. When it is introduced without washing into a platinum crucible, concentrated sulphuric acid added, and the mixture evaporated nearly to dryness, the whole of the titanium oxide will be dissolved. On cooling the liquid and pouring it into a large volume of cold water a clear solution is obtained.

14. The *spark spectrum* and the *arc spectrum* of titanium show numerous well-marked lines, which enable titanium to be readily identified (as a small admixture) in the presence of other substances. For particulars concerning

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[1] *Zeitsch. anal. Chem.*, **47**, 426.

[2] *Ibid.*, **34**, 71.

the most important lines, *cf.* Meyer and Hauser, *Die Analyse der seltenen Erden*, p. 135.

15. For the *microchemical detection* of titanium, see Haushofer, *Mikroskopische Reaktionen*, p. 130; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 108.

SEC. 53.

10. Tantalum, Ta, 181·5.

1. *Tantalum* is a platinum-grey, very ductile metal, which is pentavalent in its stable compounds, but also occurs in tetravalent form. The specific gravity of tantalum wire is given as 16·5; the melting point is 2850 In nature tantalum almost always occurs in association with niobium in numerous minerals which are widely distributed, but only in small quantities, and must be regarded as salts of niobic acid and tantalic acid The most important of these are ferrous salts of metaniobic or metatantalic acids, and are known as niobite (columbite) or tantalite, according to which of the two acids predominates. The niobates and tantalates of the rare earths, which are also important, have already been mentioned above.

Fusion with potassium hydrogen sulphate is the best method of decomposing niobite and tantalite; on boiling the fused mass with water a residue of impure niobic and tantalic acid is left.

2. *Tantalum peroxide*, Ta_2O_2 (tantalic anhydride), is formed on igniting the hydrogel of tantalic acid; it is pure white even when heated, but when contaminated with a small amount of niobium pentoxide it becomes yellow on ignition, the colour disappearing again on cooling. When heated in the air the infusible oxide is stable and gradually becomes crystalline; its specific gravity depends upon the duration of the ignition, but is about 7·5 When strongly heated in hydrogen or carbon monoxide it is reduced to a dark coloured tetroxide, which is reconverted into the pentoxide when ignited in the air at a red heat. Tantalum pentoxide is insoluble in acids, with the exception of a mixture of concentrated sulphuric acid, hydrofluoric acid, and of very strong (70 per cent.) hydrofluoric acid, which dissolve it on heating, it is soluble in fused potassium hydrogen sulphate, but on boiling the fused mass with water complete separation of the tantalic acid takes place, this residue still containing adsorbed sulphuric acid, which cannot be removed by washing, but only by ignition with ammonium carbonate. This distinguishes it from titanium, which when fused with potassium hydrogen sulphate and treated with cold water is soluble, but the method does not effect a complete separation, since titanium, niobium, and tantalum always have a reciprocal influence upon each other in solution, poly-acids or the like being formed. Tantalum peroxide is amphoteric in its behaviour, showing considerable tendency to acid formation, whilst the cations $Ta^{\cdot\cdot\cdot\cdot\cdot}$ are stable, though not very decidedly so, in solutions of the salts.

3. *Tantalates.* Tantalum pentoxide behaves towards alkalis as the

anhydride of a weak acid. Alkali tantalates are formed by fusing the pentoxide with alkali hydroxides or carbonates, and are usually soluble in water, whilst all other tantalates are insoluble. The alkali salts, only some of which have been more fully investigated, are either metatantalates or compounds of poly-acids of the type $H_8Ta_6O_{19}$. Orthotantalates and pyrotantalates are of frequent occurrence in nature, especially as ferric, cerium, and yttrium salts. *Sodium hexatantalate*, $Na_8Ta_6O_{19}.25H_2O$, is of analytical importance, and is used for the separation of tantalum from niobium;[1] it is obtained as a residue extracting the products of the fusion with sodium carbonate or hydroxide; it is only sparingly soluble in water (1 : 493 at 15°; 1 : 162 at 100°), and is insoluble in sodium carbonate or sodium hydroxide solution. The corresponding potassium salt is fairly soluble in water. Hence potassium hydroxide is preferable for the fusion of tantalum pentoxide. All alkali tantalate solutions undergo pronounced hydrolytic dissociation; the addition of acid produces a precipitation of tantalic acid hydrogel; on standing for some time they become turbid through the separation of acid salts. When dialysed they yield a pure, decidedly stable tantalic acid sol, which is precipitated by means of electrolytes, and especially by means of dilute sulphuric acid or sulphur dioxide. Carbon dioxide precipitates tantalic acid gel immediately, whilst it does not precipitate niobic acid sol until after some time.[2] *Tantalic acid hydrogel* is soluble in dilute hydrochloric or sulphuric acids, incompletely soluble in the concentrated acids, but readily soluble in hydrofluoric acid and alkali fluoride solutions; when freshly precipitated it dissolves in alkali hydroxide solution, but not in ammonia solution. Speaking generally, the conditions of solubility depend largely upon the previous treatment, the degree of dryness, etc. It forms readily soluble heteropoly-acids with oxalic acid (complex compounds), in consequence of which it dissolves when boiled with a concentrated solution of oxalic acid. and in the presence of oxalate ion only incomplete precipitation takes place by hydrolysis from an acid solution. Other hydroxy acids and polyvalent alcohols have a similar action; for example, *freshly* precipitated tantalic acid gel is readily soluble in a mixture of potassium hydroxide and mannite solution.

4. *Tantalum salts.* Salts of tetravalent tantalum are not known with certainty; those of pentavalent tantalum undergo pronounced dissociation in aqueous solution.

Tantalum pentachloride, $TaCl_5$, is formed by heating the metal or a mixture of the oxide with carbon above 200° in a current of dry chlorine, or more simply by heating the oxide in absolutely dry carbon tetrachloride or sulphur monochloride vapour. It is a yellow, solid, crystalline mass, which melts at 211°, and can be sublimed; it is decomposed by water, with the separation of tantalic acid, is completely soluble in sulphuric acid, almost completely in hydrochloric acid, and is partially soluble in potassium hydroxide solution. Acids bring about solution by checking the hydrolysis, and potassium hydroxide by the formation of tantalate ion. If the tantalum pentoxide contains titanium dioxide, titanium tetrachloride, which is volatile and fumes strongly on exposure to the air, is produced during the preparation of the chloride. Tantalum does not form an oxychloride.

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[1] Weiss and Landecker, *Zeitsch. anorgan. Chem.*, **64**, 65; Wedekind and Maass, *Zeitsch. angew. Chem.*, **23**, 2314

[2] *Cf.* Hauser and Lewite, *Zeitsch. angew. Chem.*, **25**, 100.

When tantalic acid is dissolved in hydrofluoric acid *tantalo hydrofluoric acid* is produced; on adding potassium ion the salt tantalum potassium fluoride, crystallising in rhombic needles, is obtained. This is only sparingly soluble in water (1 : 200 at 15°), and is particularly important for the separation of niobic acid. Corresponding alkali tantalum fluorides are also produced by fusion with *alkali hydrogen fluoride*. When the aqueous solution is boiled, an insoluble basic salt, $(Ta_4O_5F_{14})K_4$, separates. *This is a most certain reaction for tantalum* (Marignac). Potassium tantalum fluoride is scarcely volatile when heated, and its solutions after acidification with sulphuric acid may, therefore, be evaporated, and the residue ignited without loss, since concentrated sulphuric acid causes separation of tantalum pentoxide.

5. *Reactions of an acidified solution containing tantalic acid.*

(*a*) *Ammonia and Ammonium Sulphide* precipitate tantalic acid gel.

Hydroxy acids or polyvalent alcohols (tartaric acid, mannitol) inhibit the precipitation, and cause freshly precipitated gel to redissolve in presence of excess of alkali (suitable method for the purification of tantalic acid gel from ferric oxide, lead sulphate, etc.).

(*b*) When a solution containing excess of *hydrofluoric acid* is *boiled* an insoluble basic salt is precipitated (Marignac).

(*c*) *Gall-nut tincture* produces a light brown coloration, but only after acidification in the case of alkaline solutions.

(*d*) *Potassium ferrocyanide* produces a yellow coloration, which, however, does not appear in the presence of arsenic acid, oxalic acid, or hydroxy acids.

(*e*) A reduction (and change in colour) is *not* produced by zinc in acid solution. (Distinction from titanate and niobate ions.)

(*f*) *Hydrogen peroxide* does *not* produce a yellow coloration (distinction from titanate, cerium, and niobate ions); the resulting colourless pertitanate is readily soluble, so that a mixture of sulphuric acid and hydrogen peroxide always dissolves tantalic acid gel without difficulty. (Method to be used for separation from lead sulphate.)

6. *Alkali phosphate* dissolves tantalum pentoxide in the outer flame forming colourless beads, which have also the same appearance while hot, remain the same in the inner flame, and do not become blood-red on the addition of ferrous sulphate. (Distinction from titanium dioxide.)

7. The microchemical detection of tantalum is based upon the observation of the minute crystals in which potassium tantalum fluoride, and sodium tantalate can be obtained (Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 143; Haushofer, *Mikroskopische Reaktionen*, p. 104).

Sec. 54.

11. Niobium, Nb, 93·5.

1. In the pure condition niobium is a manganese-grey, fairly ductile metal having a specific gravity of 12·7, and melting at 1950°. It occurs in its compounds in the di-, tri-, tetra-, and pentavalent condition, but only pentavalent niobium is of essential importance. With regard to its occurrence and the decomposition of niobium minerals reference may be made to the statements about tantalum, in association with which it is almost always found.

2. *Niobium pentoxide*, Nb_2O_3, is white, can be obtained in crystalline form, and when heated becomes transitorily yellow. (Distinction from tantalum pentoxide.) Its specific gravity is 4·53. (Distinction from tantalum pentoxide and means for the approximate estimation of the relative amounts of both oxides in admixture.) When strongly ignited in hydrogen it yields black niobium tetroxide, Nb_2O_4, whilst when fused with magnesium it is converted into the trioxide, Nb_2O_3. The conditions of solubility and chemical properties of niobium pentoxide correspond to those of tantalum pentoxide given above, and accordingly niobium is also amphoteric in its behaviour.

3. *Niobates* in their general behaviour and mode of formation are completely anologous to the corresponding tantalates. When the product of the fusion with sodium carbonate is extracted a residue of sodium metaniobate, $NaNbO_3.3H_2O$, is left; this is more than twice as soluble (1 : 200 at 15°, 1 : 75 at 100°) as the corresponding sodium hexatantalate formed under the same conditions, so that a method of separation may be based on this difference in solubility. Niobic acid sol may be distinguished from tantalic acid sol by only being precipitated by carbon dioxide after a considerable time. The greater stability of niobic acid sol is also shown by the fact that the hydrogel is less readily precipitated on the addition of dilute acids, and that after precipitation it is more soluble in concentrated acids than tantalic acid hydrogel. When absolutely pure niobic acid is fused with potassium hydrogen sulphate, and the mass dissolved in water, a sol, which is not coagulated even on long-continued boiling, is obtained (Meyer and Hauser, *loc. cit.*, p. 183), but the presence of a small amount of tantalic acid causes the precipitation of a granular, sparingly soluble gel containing adsorbed sulphuric acid, and this is usually obtained on extracting with water the product of the fusion with potassium hydrogen sulphate, since the two acids nearly always occur in association. In the complete absence of tantalic acid the precipitation of niobic acid gel may be effected by the introduction of sulphur dioxide.

4. *Niobium salts* closely resemble tantalum salts in their genera behaviour, the principal points of difference being as follows: *Niobiun pentoxide*, which forms yellow prismatic needles, melting at 194° an boiling at 240·5°, is prepared in the same way as tantalum pentachloride but there is also simultaneously formed an oxychloride $NbOCl_3$, whic sublimes at 400° without melting; this volatile basic chloride is als

formed by heating the pentoxide, Nb_2O_5, with vapours of the pentachloride or in a current of hydrogen chloride. When $NbCl_5$ vapours are passed through a red-hot tube they are decomposed into chlorine and black non-volatile vapours of niobium trichloride, $NbCl_3$, which are not decomposed by water. Niobium pentachloride is decomposed by water, niobic acid being separated, and more or less niobium ion, according to the conditions, being dissolved. When boiled with hydrochloric acid and subsequently treated with water, both the chloride and oxychloride yield clear solutions, which do not give a precipitate with sulphuric acid in the cold. (Distinction from the solutions of the corresponding tantalum salts, which are readily precipitated.)

Normal *potassium niobium fluoride*, $K_2(NbF_7)$, is produced on adding potassium ion to a solution of niobic acid in hydrofluoric acid containing an excess of the latter acid, the salt is somewhat more soluble than the corresponding tantalum compound $K_2(TaF_7)$, which is isomorphous with it. Solutions containing less hydrofluoric acid yield potassium niobium oxyfluoride, $K_2(NbOF_5).H_2O$, which crystallises in nacreous plates and is soluble in 12.5 parts of water. A method of separation might be based on the considerable difference in solubility of potassium titanium fluoride (1 : 96 at 15°) and potassium tantalum fluoride (1 : 200 at 12°), if it were not for the fact that the two salts crystallise isomorphously, which makes a complete separation in this way impossible. When solutions of potassium niobium oxyfluoride are boiled, more strongly basic but, as a rule, more soluble compounds are formed by hydrolysis (important distinction from tantalum), after 12 hours' boiling, with renewal of the evaporated water, Kruss and Nilson[1] obtained a deposit of microcrystalline niobium dioxyfluoride. When a boiling, very dilute solution of niobium in hydrofluoric acid is treated with dilute potassium hydroxide solution until the colour of red litmus paper begins to change, and the neutralisation completed with ammonia, niobic acid gel is completely precipitated. (Distinction and method of separation, though only an incomplete one, from titanium, Demarçay.[2])

5. *Reactions of an acidified solution containing niobic acid.*

(*a*) *Ammonia* and *ammonium sulphide* give a precipitate of niobic acid hydrogel containing adsorbed ammonia.

(*b*) *Potassium ferrocyanide* produces in solutions of niobic acid a yellowish-white precipitate, the formation of which is prevented by arsenic, oxalic, tartaric, and citric acids, owing to these acids forming complex compounds.

(*c*) *Gall-nut tincture* produces an orange-red coloration[3] in acid solutions of niobic acid, but the presence of even a small amount of tantalum masks the colour.

(*d*) *Potassium thiocyanate*, and *zinc* and *hydrochloric acid* give a permanent golden-yellow coloration with solutions of niobic acid. (Distinction from tantalic acid and titanic acid, Pennington.[1])

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[1] *Ber.*, **20**, 1689.

[2] *Jahresber. Fortschr. Chem.*, 1885, 1929.

[3] With regard to the colour reactions with morphine, etc., mentioned by Levy, which are stated to be given by niobic and tantalic acid as well as by titanic acid, see the remarks on titanic acid in 8

(*e*) *Reducing agents* (*e.g.* zinc or tin in hydrochloric or sulphuric acid solution) produce blue or brown colorations through the formation of compounds of lower stages of oxidation. In the presence of fluorides no coloration is usually obtained, owing to the formation of complexes. Zinc and *concentrated* hydrochloric acid, however, immediately produce a brownish-violet coloration in a boiling solution of potassium niobium oxyfluoride, and this may also be used for a colorimetric estimation of niobium. Titanic acid under the same conditions only produces a faint green coloration after a considerable time, and thus, if present, a large quantity may interfere with the reaction. (*Most certain test for niobium.*)

(*f*) *Hydrogen peroxide* gives a yellow coloration with niobic acid hydrate, owing to the formation of perniobic acid. The hydrochloric acid solution of niobic acid, when treated with hydrogen peroxide and allowed to stand, gives a yellow precipitate of perniobic acid. Potassium niobium oxyfluoride, ($K_2NbOF_5.H_2O$), when treated in hot aqueous solution with hydrogen peroxide yields a white precipitate of potassium fluoroperniobate, ($NbO_2F_3.2KF.H_2O$), in the form of white scales. This compound gives a yellow coloration when treated with sulphuric acid in the presence of hydrogen peroxide. (A very sensitive reaction even in the presence of much tantalum.) Melikow and Jeltschaninow, *Chem. Zentralbl.*, 1905, I., 1276.

(*g*) *Potassium ferrocyanide* produces a yellowish-white precipitate, the formation of which is not prevented by arsenic, oxalic, tartaric, or citric acids.

(*h*) *Gall-nut extract* produces an orange-red coloration.

(*i*) *Alkali phosphate* dissolves niobium pentoxide readily, forming in the outer flame a bead, which so long as it is hot is colourless, whilst the bead obtained in the inner flame has a violet-blue or brown colour, according to the quantity of the oxide added, and is red after the addition of ferrous sulphate.

(*k*) The *micro-chemical detection* of niobium is based upon the production of minute crystals of sodium niobate (Haushofer, *Mikroskopische Reaktionen*, p. 104; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 141).

SEC. 55.

Summary and Remarks on Rare Members of Group III

The separation of the rare members of the third group from one another and from aluminium chromium and members of the fourth group, which separate simultaneously with them in the course of the analysis, is described in Chapter III. of the second part of this book (No. 60), where it is shown how they may be separated in the form of sub-groups. In this section, therefore, it is only necessary to give the most important methods for the separation of the members of the different sub-groups from one another, so far as this is possible, by means of ordinary qualitative analysis, whilst reference may be made to the information given in the preceding sections in deciding as to which other elements the individual reactions might also apply. It may once more be emphasised that a number of these rare elements cannot be separated all from the others, or detected in their presence by the ordinary method of qualitative analysis

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[1] *J. Amer. Chem. Soc.*, **18**, 38.

1. **Earth metal acids.** The mixture of the three gels of titanic, niobic, and tantalic acids, as obtained by fusion with alkali hydrogen sulphate, dissolving the fused mass in water and boiling the solution,[1] is washed with water slightly acidified with sulphuric acid and containing a little sulphur dioxide If, as may be the case, in the examination of the product of the fusion of a mineral with potassium hydrogen sulphate, it is necessary to remove admixed gangue or incompletely decomposed particles, either of the following methods may be used: (*a*) The substance is treated with a mixture of equal parts of 10 per cent. sulphuric acid and 3 per cent hydrogen peroxide, whereby the gels of the three earth metal acids (and also any ferric oxide, stannic oxide, tungstic acid, and zirconium oxide present) are dissolved, the solution is filtered, and the three gels reprecipitated by boiling from the filtrate which has been greatly diluted and treated with sulphur dioxide; or (*b*) The freshly precipitated gels are dissolved off the filter by means of an alkaline solution of mannite (15 to 20 per cent KOH, 10 per cent of mannite). Any traces of ferric and lead ions in the filtrate are precipitated from the alkaline solution by means of ammonium sulphide, and the three earth metal acids are then reprecipitated by boiling the solution after acidification with sulphuric acid and the addition of sulphur dioxide.

The following methods may be used for the separation of earth metal acid gels which have been freed in this way from impurities [1].—

A. *Separation of Titanium from Niobium and Tantalum*

(*a*) The different capacity to undergo hydrolysis in sulphuric acid solution affords a means of separation, in which, however, only part of the niobic acid is precipitated in the cold, and invariably carries down with it some titanic acid.[2]

(*b*) The mixture of the three gels is dissolved in dilute hydrofluoric acid, and the solution, which should contain only a very small amount of free hydrofluoric acid (a large excess materially increasing the solubility of the potassium tantalum fluoride) is boiled for a considerable time. The whole of the tantalic acid is left as basic double fluoride, $(Ta_4O_5F_{11})K_4$, in the residue, whilst titanium and niobium double fluorides remain in solution.

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[1] Complete separation of zirconic acid is not always effected by hydrolysis on boiling the sulphuric acid solution Streit and Franz (*J prakt Chem.*, **108**, 75) obviate the simultaneous precipitation of zirconic acid by treating the sulphuric acid solution with an equal volume of acetic acid and boiling it for 8 to 10 hours.

[2] *Cf.* Part II., Chap III, No 60.

This method, which originated with Marignac, may be used both for the separation of small amounts of titanic acid from tantalic acid, and is also of primary importance for the separation of niobic and tantalic acids.

(*c*) The mixture of the three acids is fused with sodium carbonate (also as suggested by Marignac), whereby poly- or metatantalates, soluble in water, are formed, whilst the titanic acid remains undissolved on treating the fused mass with water. The presence of the other two acids, however, reduces the insolubility of the titanic acid to some extent, so that this method, too, does not effect a complete separation. Nor does the addition of a little sodium nitrate to the clear mass, when in a state of uniform fusion (Weiss and Landecker [1]), prevent a considerable quantity of titanic acid from dissolving, whilst, on the other hand, the residue of titanic acid invariably still contains niobic acid (Hauser and Lewite [2].)

(*d*) The mixture is fused with four to five times its quantity of potassium carbonate, the mass dissolved in water at about 60°, and the solution treated with salicylic acid in the proportion of about three times the quantity of potassium carbonate used, and boiled for 3 to 4 hours, whereby the whole of the titanic acid is dissolved, whilst insoluble compounds of tantalum and niobium remain undissolved. By igniting the residue, fusion with potassium hydrogen sulphate, etc., both acids are obtained in a fairly pure condition.

(*e*) A method which is usually too involved, at all events for qualitative analysis, is that of Knop,[3] which depends upon the greater volatility of titanium tetrachloride. If a current of carbon tetrachloride is made to act upon a mixture of the three earth metal acids, heated to redness in a quartz tube, the whole of the titanium tetrachloride (boiling point 135°) distils into a connected receiver when the end of the tube is heated to a suitable temperature, whilst the chlorides of niobium and tantalum, boiling at 240·5° and 241·6° respectively, remain behind.

B. *Separation of Niobium and Tantalum from one another.*

After removal of the titanic acid, so far as this is possible by the methods given in (*a*) to (*d*), or in cases where that acid is not present, the niobium may be separated from the tantalum as follows:—

(*a*) The process outlined above in A (*b*), which is based on the insolubility of the basic potassium tantalum fluoride precipitated on boiling the solution, is a very trustworthy method.

(*b*) A method is based on the sparing solubility in sodium carbonate solution of sodium hexatantalate, obtained by fusion of the mixture with sodium carbonate. In the process of Weiss and Landecker,[1] as modified by Hauser and Lewite, the mixed acids are fused with the smallest possible quantity of sodium carbonate and the fused mass taken up with a little hot water; the greater part of the tantalum remains insoluble (as $Na_8Ta_6O_{19} \cdot 25H_2O$), and is filtered[4] off and washed with sodium hydrogen carbonate solution. As the hexaniobate is not very soluble, considerable attention must be paid to the process of solution and washing, and even then the residue will invariably contain some niobate; in order to separate this, at all events to some extent, the fusion should be repeated. The small amount of tantalic acid remaining in solution may be precipitated as hydroxide by the introduction of carbon dioxide (Sec. 53, 3), but must be filtered off not later than an hour after precipitation.

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[1] *Zeitsch. anorgan. Chem.*, **64**, 65.

[2] *Zeitsch. angew. Chem.*, **25**, 103.

[3] *Zeitsch. f. Kristallographie*, **1**, 284.

[4] *Loc. cit.*

For the identification of the earth acid metals separated by the preceding methods reference may be made to the reactions described in Secs. 52, 53 and 54, but it may be emphasised once more that the most trustworthy test for *tantalum* is the precipitation of the double basic fluoride from a boiling solution (Sec. 53, 4). Niobium may be detected with some degree of certainty in the presence of minute quantities of titanium by the behaviour of its potassium oxyfluoride towards zinc and concentrated hydrochloric acid (Sec. 54, 5 (c). This reaction is also much more trustworthy for its detection in the presence of tantalum than the different coloration obtained with gall-nut tincture (Secs. 53, 5 (c), and 54, 5 (c). The yellow coloration obtained with hydrogen peroxide, which is described in detail in Sec. 52, 9, affords a most certain reaction for titanium, whilst the colour reaction with chromotropic acid, given in Sec. 52, 8, and that with pyrocatechol are also extraordinarily sensitive.

2. **The separation from aluminium, chromium, and beryllium**, which are obtained together in *one* sub-group in the course of the analysis (*cf.* Part II., Chap. III., No. 60, 4 and 5), has already been dealt with above (Sec. 42), so far as concerns the two first. By taking advantage of the different behaviour of the potassium hydroxide solutions of the substances on boiling, it is possible, provided that the liquid is sufficiently dilute, to precipitate beryllium hydroxide and chromic hydroxide together, and to separate the former by means of one of the methods outlined in Sec. 42, which depend upon the oxidation of the chromic ion, followed by precipitation of the beryllium ion as hydroxide. If the aluminium and beryllium ions are first separated together from chromium by oxidation of the latter, the resulting *aluminium* and *beryllium* hydroxides may then be separated by means of the reactions described in detail in Sec. 43, 3, 4, 5, 7, and 9. The crystalline precipitate obtained with diammonium hydrogen phosphate affords the best means of identifying beryllium ion (Sec. 43, 5).

3. **Separation of ceria and yttria earth metals as oxalates.** *Their separation from thorium on the one hand, and from zirconium, beryllium, aluminium, and chromium, and also from members of the fourth group on the other hand.*

In the analytical process all the members of the third and fourth groups are obtained together in one precipitate. When this is dissolved in acid the ions of the ceria and yttria earth metals, together with thorium ion, may be precipitated from the solution (if necessary after separation of earth metal acids, Part II., Chap. III., No. 60, 4) as oxalates, and the members of the fourth group, together with aluminium, chromic, beryllium, and zirconium ions, obtained in solution. The thorium may be extracted from the precipitate by means of hot ammonium oxalate solution (Part II., Chap. III., No. 60, 5).

4. **Separation from thorium (zirconium, tetravalent cerium, and titanium), from trivalent ceria earth metals, and from yttria earth metals.**

(*a*) Sodium thiosulphate, (*b*) potassium iodate in acid solution, and (*c*) sodium hypophosphate precipitate **thorium,** *zirconium,* and *ceric ions,* and also *titanium ion.*

Simultaneous precipitation of ceric ion can usually be prevented by previous reduction to the trivalent form. For the methods of separating thorium ion from the other ions simultaneously precipitated by these reagents, or of preventing the precipitation of these ions, reference may be made to the individual reactions in question in Sec. 44 (especially 5).

Scandium ion behaves like thorium in the thiosulphate reaction. It is also precipitated by potassium iodate, but the precipitate is soluble in nitric acid.

(*d*) *Hydrogen peroxide* precipitates *thorium ion* from neutral and slightly acid solution, whilst it also precipitates zirconium ion more or less completely, according to the nature of the anion present. Ceric ion may be partly reduced to the trivalent condition and partly converted into the tetravalent condition. In the latter form it is precipitated as hydroxide by ammonia.

5. **The behaviour of the sulphates or double sulphates** may afford a means of separating *thorium ion* from the ions of the other rare earth metals (Sec. 44, 7). On the other hand, the double sulphates may be used for the *separation of the yttria and ceria earth metals*, and also for the separation of the individual members of these sub-groups, but the process is a preparatory one rather than a method of analytical separation.

6. **The double nitrates** may be used in a process of fractional crystallisation for purifying the different elements, but are not suitable for analytical separation in the ordinary meaning of the term.

7. **The separation of cerium from the rest of the ceria earths** may be effected by methods based upon its conversion into the tetravalent form and the different reactions which it then gives (*cf.* 4). One of the following methods, for example, may be used for the oxidation and separation of cerium:[1] (*a*) The acid solution of the chlorides of the ceria earth metals is nearly neutralised, without, however, causing a permanent precipitate to be formed, a sufficient quantity of sodium acetate, and an excess of sodium hypochlorite added, and the whole boiled for some time; under these conditions ceric ion is precipitated as basic ceric acetate (which must be washed with sodium acetate solution (Popp and Erk), whilst the remainder of the ceria earth ions, with traces of ceric ion, remain in solution (Popp, *Ann. Chem. Pharm.*, **131**, 360)).

(*b*) The solution is treated with potassium hydroxide, the precipitate washed and suspended in potassium hydroxide solution, and a current of chlorine introduced. Ceric hydroxide is left undissolved, whilst the other ceria earth metals dissolve as chlorides or hypochlorites (Nosander, Damour, and St. Clair Deville, *Comptes rend.*, **59**, 272; *cf.* also Drosbach, *Ber.*, **35**, 1826). The residual precipitate is very impure, so that only by frequent repetition of the process can a complete separation be effected. The method may be of use, however, for the separation of small amounts of cerium.

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[1] See also the detailed description in R. J. Meyer and Abegg's *Handbuch*, Vol. III., Part I., p. 179 *et seq.*

(*c*) The mixture is dissolved in an excess of strong nitric acid, the solution boiled with lead peroxide, and the resulting orange-yellow liquid evaporated to dryness. The residue is then heated until part of the acid has evaporated, treated with water, acidified with nitric acid, and the insoluble residue of basic ceric nitrate separated from the solution, which will contain all the lanthanum and didymium (Gibbs, *Zeitsch. anal. Chem.*, **3**, 396). In using this method it should be noted that the lead ion must be removed by means of hydrogen sulphide from both the residue and the solution before they are subjected to further treatment. According to Knorre the oxidation of the ceric ion is incomplete; *bismuth* tetroxide and nitric acid oxidise it completely (Wagner and Muller).

(*d*) The solution is treated, while continually stirred, with a solution of sodium peroxide in ice-water; the reddish-brown precipitate is washed by decantation with hot water, and, after the liquid has been drained off by suction, is dissolved in nitric acid. On adding ammonium nitrate the cerium may then be precipitated as ceric ammonium double nitrate (Mengel, *Zeitsch. anorgan. Chem.*, **19**, 67). Pissarjewski recommends the addition of hydrogen peroxide and of ammonia, both in the cold, to the acid solution; this effects complete oxidation and on subsequent boiling of the liquid complete precipitation of the cerium as ceric hydroxide, which may then be treated as described above.

The *presence of cerium* may be detected by the yellow to red coloration of its compounds in all cases in which it occurs in the tetravalent form. If these colorations are not directly visible in a substance which is only to be tested for cerium without separating it, oxidation by means of persulphate in acid solution may be used, in addition to the above-mentioned reactions, and the resulting ceric ion may then be recognised by its yellow coloration.

For the detection of small quantities of cerium it is advisable to employ the reaction described in (*d*), by adding dilute ammonia solution to the acid solution of the earth metals until a permanent precipitate is just formed, and then adding the hydrogen peroxide. Under these conditions the precipitate of hydroxide, enriched by the partial precipitation of cerium, will show a distinct yellow coloration, whilst in the absence of cerium it will have a bluish-white appearance.

8. **Neodymium** and **praseodymium** and the other so-called "coloured" earth metals may be readily and certainly detected by means of their absorption spectra

FOURTH GROUP.

Ions of the Heavy Metals, the Sulphides of which are soluble in Acids.

Members of frequent occurrence: **Zinc, Manganese, Nickel, Cobalt, Iron** (as ferrous and ferric ions)

Members of less frequent occurrence: **Uranium, Thallium, Indium, Gallium, Vanadium.**

SEC. 56.

CHARACTERISTICS OF THE GROUP.

Position in the periodic system.—All the members of the fourth analytical group are pronounced heavy metals Most of them occupy a place in the middle of the first great period, in which they directly follow one another from vanadium to gallium in a series interrupted only by chromium and copper, with gallium are associated the analogous higher members of the third group of the periodic system, indium and thallium Lastly, uranium, which also belongs to the fourth analytical group, occupies a position in the periodic system far removed from the others, but from an analytical point of view, however, only the properties of the cation UO_2 are of importance, and these agree closely with those of the rest of the ions of the group In accordance with their position in the periodic system the members of frequent occurrence all show great similarity in their behaviour. They all occur mainly in a divalent form, in which they are also so positive that they show only the slightest, if any, tendency towards hydrolysis. The individual members do not differ very greatly as regards their positive character. Manganese is the most strongly electro-positive, zinc the next, and then iron, cobalt, and nickel, which also are particularly close to one another in their order of tension Zinc occurs only in the divalent form, and has an amphoteric character, whilst the four others are only met with as cations in the divalent form. These four also occur in the trivalent form (iron in very important compounds) In this form they are slightly positive, show a tendency towards hydrolysis, and combine with oxygen to form anions. Manganese, iron, and to a less extent also cobalt and nickel, occur in still higher forms of valency, in which their tendency to combine with oxygen to form acid radicles is shown to a still more pron[illegible]d extent. In this respect vanadium closely resembles th[illegible]ivalent form they show many close

detailed descr[illegible] p. 179 *et seq.*

similarities with the members of the third analytical and periodic group, to which latter gallium, indium, and thallium also belong.

The four metals which stand next to each other, manganese, iron, nickel, and cobalt, show in some cases a particularly pronounced tendency to form complexes, and in this respect vanadium agrees with them.

Analytical character of the group.—The ions of the fourth *analytical group* are *not precipitated* by *hydrogen sulphide in the presence of a considerable amount of hydrogen ions* (*i.e.* from solutions which contain a sufficient quantity of free acid) Hydrogen sulphide precipitates the ions of the fourth group either *not at all* or *incompletely*, or only under very definite conditions completely *from slightly acid or neutral solutions* (in which hydrogen ions are formed through the decomposition of the metal salts by the hydrogen sulphide), but, on the other hand, *hydrogen sulphide* precipitates them completely from *alkaline solutions*, and *alkali sulphide* precipitates them from *alkaline or neutral solutions.*[1] The resulting precipitates, hydrated *sulphides*, are insoluble in water,[2] some are easily soluble in dilute acids, and others (nickel and cobalt sulphide) are insoluble, whilst *most of them are insoluble*, some (nickel sulphide) under certain conditions slightly soluble or even completely soluble (vanadium sulphide) in solutions of *alkali sulphides*.

The ions of the fourth group are, therefore, distinguished from those of the first group by the fact that they are precipitated from their solutions by ammonium sulphide; from those of the second group by the fact that they give precipitates with ammonium sulphide, whilst the ions of the second group are not precipitated, or are only precipitated in the presence of certain anions (*e g* phosphate ion), and then in the form of insoluble salts (phosphates, borates, etc); and from the ions of the third group by the fact that the precipitates produced by ammonium sulphide are sulphides, and not (as in the case of aluminium ion, chromic ion, etc) hydroxides. The hydroxides, carbonates and phosphates of the elements of the fourth group are insoluble in water.

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[1] For the very characteristic behaviour of vanadium, see Sec. 68, 4 It is doubtful whether gallium is really precipitated as sulphide, since it is only precipitated simultaneously with other metals. Possibly it would be more correctly included in the third group (*cf.* Sec 67).

[2] That is to say, practically insoluble, since their solubility is always still about a hundred times as great as that of the sulphides of the fifth analytical group; on this fact depends the difference between the behaviour of the two groups in acid solution, in which, in the case of the sulphides of the fourth analytical group, the extremely slight concentration of the S'' ions is no longer sufficient to exceed the solubility product (*cf.* also the references quoted on p 116, and **Part II., Chap. III., No. 18**; also p. 219).

c

SPECIAL REACTIONS OF THE MEMBERS OF FREQUENT OCCURRENCE

SEC. 57.

(a) **Zinc,** Zn, 65·37

1. *Zinc is divalent.* It has a specific gravity of 6·9 to 7·2, and melts at about 419°. In the *metallic condition* it is bluish-white, highly lustrous, and when exposed to the air becomes coated with a thin layer of basic zinc carbonate. It is of medium hardness, ductile between 100° and 150°, but otherwise more or less brittle; it readily melts on charcoal in the blowpipe flame, and afterwards boils (boiling-point 929°), and burns with a bluish-green flame, producing white fumes in the air, and coating the charcoal with oxide. *Pure* zinc is scarcely soluble in dilute hydrochloric or sulphuric acid, but dissolves in very dilute nitric acid with the evolution of nitrous oxide, and in concentrated nitric acid with the evolution of nitric oxide. *Impure* zinc, or zinc in contact with metals of similar electrolytic solution tension, dissolves in dilute hydrochloric or sulphuric acid, with the evolution of hydrogen, $Zn+2H=Zn+H_2$; for example, $Zn+H_2SO_4=ZnSO_4+H_2$. Zinc is also soluble in solutions of alkali hydroxides, hydrogen being liberated and zincate ion formed, $Zn+2OH'=ZnO''_2+H_2$; for example, $Zn+2NaOH=Zn(ONa)_2+H_2$. Zinc is thus amphoteric.

2. *Zinc oxide*, ZnO, and *zinc hydroxide*, $Zn(OH)_2$, are usually white powders, insoluble in water, but readily soluble in hydrochloric, nitric, and sulphuric acids. Zinc oxide becomes lemon-yellow when heated, but turns white again on cooling. When ignited before a blowpipe it becomes luminous and strongly incandescent.

3. The *salts* of zinc are colourless or white, when the anion does not impart a colour; some are soluble in water, others in acids. The neutral salts, soluble in water, redden litmus in consequence of hydrolysis: the salts of volatile acids are, with the exception of zinc sulphate, which will stand gentle ignition to over 700°, readily decomposed when heated. Zinc chloride, which is volatile at a red heat, is a strongly hygroscopic deliquescent mass with a corrosive action.

4. **Hydrogen sulphide** does *not* precipitate zinc ion from its solutions, provided that they are *acidified* with a sufficient quantity

of a strong acid. If the amount of free acid is small, especially in the presence of alkali salts of weak acids (which repress the hydrogen ion concentration), a white precipitate of hydrated *zinc sulphide*, ZnS, is produced. The properties of this precipitate are described at the end of paragraph (5) Under suitable conditions the precipitation is complete. Alkali hydrogen sulphates only prevent the precipitation when present in large amount The whole of the zinc ion is precipitated from sufficiently dilute solutions acidified with weak acids [acetic and formic acids (Delffs, Hampe, Funke), thiocyanic acid (Zimmermann), monochloroacetic acid (von Berg), succinic acid (Alt and J. Schulze), or gallic acid (E. A. Lewis)], and also from very dilute sulphuric acid solutions (E. C. Sullivan and W C Taylor, *Zeitsch. anal Chem* , **49,** 597). From neutral solutions, according to the nature of the anions present, the zinc is precipitated either incompletely or completely, the latter being the case when the solution contains a sufficient quantity of an alkali salt of a weak acid (*e.g* sodium acetate). Heating to 50°–60° promotes the separation

All these conditions in connection with this and the following members of the fourth group may be explained by the fact that when through the presence of many H· ions the dissociation of the weak acid, hydrogen sulphide, is strongly repressed, sufficient S″ ions no longer remain in the solution to reach or exceed the solubility product $[Zn^{\cdot\cdot}].[S'']=K$, notwithstanding the high $Zn^{\cdot\cdot}$ concentration. With regard to the reaction equation $Zn^{\cdot\cdot}+H_2S \rightleftarrows ZnS+2H^{\cdot}$, it may be pointed out that the course of the equation is from left to right or *vice-versa*, and that hence all the conditions which reduce the concentration of the H· ions, and correspondingly increase those of the S″ anions, promote the formation and precipitation of zinc sulphide, whilst conversely the increase of H· ions, as by the addition of a strong acid, causes solution of the zinc sulphide already formed (*cf.* however the work of St. Glixelli, *Zeitsch. anorg. Chem.*, **55**, 297, in which it is shown that considerable retardation may occur in the production of equilibrium. There thus results a *false* equilibrium, whilst in the presence of catalysts such as ZnS, CuS, CdS, or after a very long time some weeks – even in fairly acid solutions, pronounced precipitation of ZnS takes place).

5 **Ammonium sulphide** *precipitates from alkaline and neutral* solutions, and **hydrogen sulphide** from *alkaline solutions*, *the whole of the zinc ion* as a *white precipitate of hydrated zinc sulphide*.[1] Ammonium chloride has a considerable influence in promoting the separation.

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[1] According to Glixelli (*loc. cit.*), this is β-zinc sulphide, which contains a larger proportion of water, and is about four times more soluble in water than α-zinc sulphide, which is formed in acid solutions, and into which it is gradually converted.

In the case of very dilute solutions, the precipitate only separates after standing for a long time. It is not soluble either in excess of *ammonium chloride solution*, or of *alkali hydroxide* or *ammonia solutions*, whilst an excess of hydrogen sulphide or of alkali hydrogen sulphide produces a colloidal solution (L. W. McCay, *Zeitsch. anal. Chem.*, **49,** 598). It is dissolved by *hydrochloric, nitric, and dilute sulphuric acids*, but not by acetic and other weak acids. Occasionally the precipitate is slimy. This colloidal condition is not produced in the presence of alkali salts of strong acids, and heating has the same effect.

6. *Ammonium thioacetate solution* does not produce a precipitate in acid solutions of zinc, but precipitates zinc sulphide from ammoniacal solutions. *Sodium thiosulphate* does *not* give a precipitate.

7. **Potassium and sodium hydroxides** precipitate *zinc hydroxide*, $Zn(OH)_2$, *from solutions of zinc salts*, in the form of a gelatinous white precipitate, which, especially when freshly precipitated, is readily and completely soluble as *zincate ion*, but with more difficulty after it has stood for some time (*i.e.* has undergone change). When these alkaline solutions are boiled they remain clear if concentrated, but if they are dilute nearly the whole of the zinc hydroxide separates as a white precipitate. Zinc hydroxide thus has the character both of a base and also, in the presence of strong bases, of an acid. The reaction $Zn(OH)_2+2OH' \rightleftarrows ZnO''_2+2H_2O$ – for example, $Zn(OH)_2+2NaOH \rightleftarrows Zn(ONa)_2+2H_2O$ therefore proceeds from right to left in dilute solutions, and this is also the case when the liquid is boiled in the presence of a sufficient excess of alkali. Ammonium chloride produces in alkaline solutions containing only a very slight excess of potassium or sodium hydroxide a white precipitate of zinc hydroxide, which redissolves on the addition of more ammonium chloride (*cf.* the following paragraph), but no precipitate is produced by ammonium chloride in solutions which contain a larger amount of potassium or sodium hydroxide. (Distinction from aluminium ion.)

8. **Ammonia** also produces in solutions of zinc salts, when they do not contain a great excess of free acid (*i.e.* show a smaller hydrogen ion concentration), a precipitate of zinc hydroxide, which is *readily soluble in excess of the precipitant*. A concentrated solution becomes turbid when mixed with water. When a concentrated solution is boiled, part of the zinc hydroxide separates, whilst the whole of it separates on boiling a dilute solution. Ammonium salts influence or prevent these precipitations. (The action of ammonium salts in this case is analogous to that described in the case of magnesium ion

(pp 34, 149), but the formation of complex ions has also to be taken into consideration here)

9. **Sodium carbonate** produces a precipitate of basic zinc carbonate, insoluble in excess of the precipitant The composition of the precipitate varies with the concentration and temperature of the solution, and, the extent to which the precipitant predominates. Ammonium salts in large excess prevent its formation.

10. **Ammonium carbonate** precipitates the same compound as sodium carbonate, and the precipitate re-dissolves on the addition of more ammonium carbonate On boiling the diluted solution a white precipitate is obtained Ammonium salts influence or prevent this precipitation.

Notes to 3, 7 to 10 · If solutions of zinc salts contain non-volatile organic acids the precipitation by alkali hydroxides and carbonates is affected or prevented, owing to the formation of complex ions; sugar, however, does not prevent the precipitation

Sodium peroxide or hydrogen peroxide, bromine, and other oxidising agents, cannot precipitate zinc from alkaline solutions of zinc salts, or alter the zinc ion, since zinc only occurs in the divalent condition. This enables the zinc ion to be separated from the ions of oxidisable metals (manganese, nickel, cobalt, bismuth) The precipitate, however, is not quite free from zinc.

11. **Barium carbonate** does not precipitate zinc carbonate in the cold from aqueous solutions of zinc salts, with the exception of zinc sulphate.

12 *Potassium cyanide* gives a white precipitate of zinc cyanide, $Zn(CN)_2$ This is soluble in excess of the precipitant, a complex anion being formed, $Zn(CN)''_4$; $Zn + 2CN' = Zn(CN)_2$; $Zn(CN)_2 + 2CN' = Zn(CN)''_4$, for example, $ZnCl_2 + 2KCN = Zn(CN)_2 + 2KCl$; $Zn(CN)_2 + 2KCN = Zn(CN)_4K_2$ If the excess of potassium cyanide is not too great, potassium or sodium sulphide precipitates hydrated zinc sulphide immediately from this solution, whilst hydrogen sulphide or ammonium sulphide precipitates it slowly and incompletely.

13 **Potassium ferrocyanide** [1] gives a gelatinous white precipitate of *zinc ferrocyanide*, $Zn_2Fe(CN)_6$, or of potassium zinc ferrocyanide, $Zn_3K_2[Fe(CN)_6]_2$, which is soluble in excess of the precipitant and sparingly soluble in hydrochloric acid. On treating this precipitate with bromine a deep yellow oxidation product is obtained (F. F.

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[1] With regard to an analogous reaction with potassium cobaltocyanide, see Sec. 60, footnote to 12.

Werner, *Zeitsch. anal. Chem.*, **51,** 481). The precipitate with ferrocyanide is also produced in a solution treated with tartaric acid and excess of ammonia solution. In the presence of even small amounts of proteins, potassium ferrocyanide produces in slightly acid solutions not a gelatinous but a flocculent precipitate. J. Brand recommends this reaction for the detection of traces of zinc ion in beer. Only the non-occurrence of a precipitate, however, proves the absence of zinc ion, whilst further tests for zinc must be applied to any precipitate obtained (*Chem. Zentralbl.*, 1905, II., 515)

14, **Potassium ferricyanide** gives a brownish-orange yellow precipitate of *zinc ferricyanide*, $Zn_3[Fe(CN)_6]_2$, which is soluble in hydrochloric acid and in ammonia solution.

15. *Potassium periodate* produces a white precipitate in aqueous solutions of zinc The presence of ammonium chloride and ammonia prevents the formation of the precipitate in the cold, or has an influence on its formation, when a large amount of zinc is present When the solution is boiled the zinc ion separates (Stanley R Benedikt, *Chem Zentralbl*, 1906, I, 501).

16. If an alkaline zincate solution is *electrolysed* in a very small electrolytic cell containing a copper wire 0·5 mm. in diameter as cathode and a platinum wire as anode, with a voltage of 10, extremely minute quantities of zinc may be separated and recognised by the colour of the copper wire (W. Neumann, *Zeitsch anal Chem.*, **49,** 597).

17. When an alcoholic or ethereal solution of *resorcinol* is added to an ammoniacal solution of a zinc salt, it gives a bright *blue coloration ;* this is a sensitive reaction, but is only distinctive in the absence of cadmium, copper, cobalt, nickel, and manganous ions (A. del Campo Cerdan, *Chem Zentralbl*, 1909, II., 474).

18. A zinc salt or a mixture of a zinc salt with sodium carbonate, exposed to the **reducing flame of the blowpipe,** coats the charcoal with a filmy deposit of zinc oxide, which, so long as it is hot, is yellow, but becomes white on cooling. The formation of this is due to the fact that the reduced metallic zinc volatilises at the moment of its production and is re-oxidised on its passage through the outer flame The deposit of metal obtained, as described on p. 89, is black with a brownish outer film, whilst the oxide deposit is white and therefore invisible on porcelain. It may be dissolved in a little nitric acid and tested as described in 19.

19. If zinc oxide or a zinc salt is moistened with a solution of **cobaltonitrate** and heated in the blowpipe flame, unfused *cobalti-*

zincate, $CoZnO_2$, which has a fine green colour (Rinmann's green), is obtained. If therefore the deposit obtained as described in test 18, or the residue left by heating the substance in the oxidising flame, is moistened with cobalt solution and ignited, it appears green when cold.

The reaction may be made very sensitive by treating the solution of a zinc salt with a very small amount of a solution of a cobaltous salt (not sufficient to colour the liquid bright red), adding a slight excess of sodium carbonate, boiling and filtering the liquid, and igniting the washed precipitate on platinum foil. On powdering the residue the green colour may be easily and unmistakably recognised (Bloxam) Minute quantities of zinc may also be detected by means of this reaction by saturating a roll of filter paper with zinc solution, which has been treated with a little cobaltous nitrate, and igniting it in a holder of platinum wire An excess of the cobaltous salt solution must be avoided, since otherwise the resulting black cobalto-cobalti oxide masks the green coloration

20. With regard to the microchemical detection of zinc ion, see Haushofer, *Mikroskopische Reaktionen*, p. 151; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 69; Schoorl, *Zeitsch. anal. Chem.*, **48**, 224, 230; H C Bradley, who recommends precipitation as zinc nitroprusside (*Chem Zentralbl.*, 1906, II., 1873); Pozzi-Escot, who recommends the use of calcium zincate (*Chem. Zentralbl.*, 1907, II., 484).

SEC. 58.

(b) Manganese, Mn, 54·93.

1. *Manganese* occurs in the di-, tri-, tetra-, hexa- and hepta-valent forms. Of the compounds in the solutions of which it is present as cation only the manganous compounds (of divalent manganese) are stable. This section therefore, deals mainly with the reactions of these.

Metallic manganese is greyish-white, slightly lustrous, very hard and brittle. Its specific gravity is about 7 2, and its melting point about 1245° to 1260°. When not quite pure, it is rapidly oxidised in moist air and also in water (with the evolution of hydrogen), and is disintegrated into a blackish-green powder. It is readily soluble in acids, forming solutions which contain manganous ion.

2. *Manganous oxide*, MnO (manganese monoxide), is light green, whilst manganous hydroxide is white. The former burns with

incandescence when heated in the air, producing *manganous manganic oxide*, Mn_3O_4, whilst the latter rapidly absorbs oxygen from the air and is converted into brown hydrated manganous manganic oxide. Both are readily soluble in hydrochloric, nitric, and sulphuric acids.

The brownish-black *manganic oxide*, Mn_2O_3, *manganous manganic oxide*, Mn_3O_4, as also black *manganese dioxide*, MnO_2, dissolve when heated with hydrochloric acid, evolving chlorine, and forming manganous chloride, whilst when heated with concentrated sulphuric acid they yield manganous sulphate, and oxygen is liberated.

Tri- and tetravalent manganese, corresponding to the two higher oxides mentioned, can also form anions in association with oxygen, so that salts are produced which are derived from manganic hydroxide and from the hydroxide of tetravalent manganese (manganite) acting as acids. All these compounds are decomposed by acids in such a way that, on the one hand, there are formed salts of those cations which were in combination with the anions containing the manganese, and, on the other hand, the same compounds are formed as are produced by the action of the acids upon manganic oxide and manganese dioxide. Little is known about the oxides of the hexa- and heptavalent manganese, MnO_3 and Mn_2O_7, in the free condition The green *manganates*, R_2MnO_4, and the red *permanganates*, $RMnO_4$, are derived from them.

All the manganous oxides are converted into manganous manganic oxide, Mn_3O_4, when ignited in the air.

3. The *manganous salts* are colourless or pink when the anion present does not impart a colour to them ; some are soluble in water, others in acids. The manganous salts of volatile acids are, as a rule, easily decomposed on ignition, but manganous sulphate can be heated to redness without decomposition. Solutions of the neutral manganous salts show a neutral reaction. The manganous ion has pronounced basic properties, and in many respects resembles magnesium ion and ferrous ion. In contradistinction to the conditions in the case of ion, manganous salts are far more stable than the compounds of the trivalent very weakly basic manganic ion, which in aqueous solution undergo pronounced hydrolysis.

4. **Hydrogen sulphide** does *not* produce a precipitate in *acid* solutions of manganous salts, even in the case of weak acids, such as acetic, formic, monochloroacetic, and succinic acids. No precipitate or, at most, a very incomplete one, is also produced in neutral solutions.

5. **Ammonium sulphide** precipitates from *neutral* and *alkaline* solutions, and **hydrogen sulphide** from *alkaline* solutions, *the whole of the manganese ion as hydrated manganous sulphide*, $MnS.H_2O$, which appears *yellowish-white* when present in small quantity, and pale *flesh-coloured* in larger quantities, becoming *dark brown* on exposure to the air through absorption of oxygen; it is insoluble in ammonium sulphide and alkali hydroxide solutions, but dissolves readily in hydrochloric, nitric, and acetic acids. The separation of the precipitate, which is colloidal at first, is considerably promoted by the addition of a moderate quantity of ammonium chloride. It only separates from very dilute solutions after they have been allowed to stand for some time in a warm place. The precipitation is retarded by ammonium oxalate and tartrate, and especially by ammonium citrate, which last also affects the completeness of the separation. If ammonia and ammonium chloride are present in considerable excess, the flesh coloured hydrated precipitate is converted rapidly on boiling, but sometimes even in the cold, into the green crystalline manganous sulphide, $3MnS.2H_2O$, which contains less water. Ammonium chloride influences or prevents this conversion. The presence of much free ammonia has an influence on the precipitation of manganous sulphide by ammonium sulphide (it may entirely prevent the precipitation by yellow ammonium sulphide containing polysulphides) (Classen, *Zeitsch. anal. Chem.*, **8**, 370). Solutions which contain much free ammonia must, therefore, first be neutralised with hydrochloric acid before adding the ammonium sulphide.

6. **Potassium and sodium hydroxide** produce *whitish precipitates* of *manganous hydroxide*, which on contact with the air become *brownish* and finally *dark brown*, owing to the manganous hydroxide absorbing oxygen from the atmosphere, and being converted into manganous manganic hydroxide and hydrated dioxide. *Ammonia* also precipitates manganous hydroxide, but the precipitate contains only about half of the manganous ion present (*cf.* the analogous behaviour of magnesium ion, pp. 31 and 149, and of zinc ion, Sec. 57, 8). Ammonia and ammonium carbonate solution do not dissolve manganous hydroxide. *Ammonium chloride*, however, when added in sufficient quantity, completely *prevents the precipitation* of manganous salts from their solutions by means of *ammonia*, and partly prevents the precipitation by potassium or sodium hydroxide. In the case of precipitates already formed, only those portions which have not yet been oxidised into a higher state of oxidation are dissolved by ammonium chloride solution. Ammoniacal solutions of divalent

manganese become brown on exposure to the air, and yield a deposit of dark brown manganous manganic hydroxide. Even in the presence of ammonium chloride, solutions of manganous salts which have been treated with ammonia become turbid on exposure to the air, owing to the separation of higher manganous oxides. If, however, the solution is first treated with hydroxylamine hydrochloride (or a hydrazine salt) this oxidation is prevented, and the liquid remains clear (Elber, *Zeitsch. anal. Chem.*, **47,** 671). Manganous manganic hydroxide is soluble in a solution of *potassium hydrogen oxalate*, forming a fine *red* solution containing a complex manganese oxalate ion.[1]

7. On treating a solution of a manganous salt with **potassium** or **sodium hydroxide** or **ammonia** and adding a solution of **bromine** or **hydrogen peroxide,** *the whole of the manganese separates as brownish-black hydrated manganese dioxide*, with a composition approximating $MnO(OH)_2$. The separation is promoted by heat. Solutions of manganous salts which have been treated with sodium acetate also give a precipitate when heated with bromine.

Sodium peroxide acts in the same way. *Persulphates*, *e.g.* ammonium persulphate, give no precipitate in the cold, but on boiling the solution hydrated manganese dioxide is precipitated. In the *presence of a small amount of a silver salt* oxidation to *permanganate* takes place, so that a *violet coloration* instead of a precipitate is produced. In making this test only a very minute quantity of silver salt must be used, very little free acid must be present, and it is best to allow the liquid to stand at a moderate temperature. In this form the reaction is *very sensitive*. If too much silver salt or too much nitric acid is present a brown coloration due to silver peroxide is produced, but this disappears on boiling the liquid. If much manganese is present a permanent precipitate of manganese dioxide is obtained, in addition to the red coloration (Marshall, *Zeitsch. anal. Chem.*, **43,** 418).

Notes to 6 and 7: Non-volatile organic acids may affect or even prevent the precipitation of hydrated manganous hydroxide or manganese dioxide. *Sugar* influences or prevents the precipitation of the manganese as manganous hydroxide, but not as hydrated manganese dioxide.

8. **Ammonium carbonate** gives a white precipitate of manganese carbonate, $MnCO_3 + H_2O$. The precipitation is complete after some

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[1] This reaction has been recommended by Sacher for the detection of *very* small quantities of manganese (*Chem. Zeit.*, **39**, 319).

time, even in the presence of ammonium chloride. **Potassium or sodium carbonate** produces a white precipitate, which, according to the conditions, is hydrated manganous carbonate, manganous hydroxide, or a mixture of the two. In the freshly precipitated condition it is soluble in ammonium chloride solution; it does not dissolve in excess of the precipitant.

Guanidine carbonate behaves in the same way as ammonium carbonate (Grossmann and Schück, *Chem. Zeit.*, **30,** 1205).

Note: *Non-volatile organic acids* influence or prevent the production of precipitates by potassium or sodium carbonate, and retard but do not prevent the precipitation by ammonium carbonate.

9 **Barium carbonate** does *not* precipitate manganous ion from aqueous solutions when digested with them in the cold. The only exception to the rule is manganous sulphate.

10 *Potassium cyanide* produces a brownish-yellow precipitate of *manganous cyanide*, $Mn(CN)_2$, which turns brown in the air, it is soluble in excess of potassium cyanide solution, forming a yellow solution which contains the manganese in the form of manganous cyanide ion, $Mn(CN)''''_6$ This ion is only stable in the presence of a considerable excess of potassium cyanide. When diluted the liquid becomes green owing to the formation of the ion $Mn(CN)_3$. On boiling the diluted yellow solution the manganous cyanide ion is decomposed, manganous hydroxide being separated:

$$Mn(CN)''''_6+2H_2O=6CN'+2H^{\cdot}+Mn(OH)_2$$

Ammonium sulphide does not precipitate manganous sulphide in the presence of a large excess of potassium cyanide, but the precipitate is produced on heating the diluted solution.

11. **Potassium ferrocyanide** produces a white precipitate of *manganous ferrocyanide*, $Mn_2Fe(CN)_6$, which dissolves with difficulty in hydrochloric acid The precipitation also takes place from a freshly prepared ammoniacal solution of a manganous salt which has been treated with tartaric acid (Distinction from ferric ion, L. Blum.)

12 **Potassium ferricyanide** produces a brown precipitate of *manganous ferricyanide*, $Mn_3[Fe(CN)_6]_2$, which is only slightly soluble in strong hydrochloric acid and insoluble in ammonia solution When boiled with a large excess of concentrated hydrochloric acid the precipitate is decomposed and dissolves.

13 When a small quantity of a solution of a manganous salt *free from chloride* is dropped on to **lead peroxide,** dilute *nitric acid free from chloride* added, and the mixture boiled and allowed to

settle, the liquid becomes *deep red*, owing to the formation of permanganate ion (Hoppe-Seyler[1]).

14. *Potassium bromate* produces, even in the cold, a violet coloration in a sulphuric acid solution of a manganous salt. Potassium chlorate and iodate do not give the reaction (Vitali, *Chem. Zentralbl.*, 1898, II., 942).

Potassium chlorate produces a precipitate of hydrated manganese dioxide on boiling a *nitric acid solution* of a manganous salt.

15. *Potassium periodate* produces immediately in solutions of manganous salts a dark red precipitate, or, in the case of very dilute solutions, only a red coloration The precipitate is probably a manganous periodate. It is dissolved by hydrochloric acid, with the liberation of chlorine. Sodium hydroxide converts it immediately, and ammonia after some time, into black hydrated manganese dioxide. The reaction, which is very sensitive, is promoted by heat

16. When a manganese compound is dissolved in *fuming hydrochloric acid*, and one or two drops of *strong nitric acid* or a small amount of a *nitrate, chlorate, hypochlorite, chromate*, or *lead peroxide* added, the solution, on heating, shows a greenish-black coloration, which disappears on continuing the heating, or on diluting the liquid. It depends upon the formation of *manganese tetrachloride*, $MnCl_4$ Perchlorates, bromates, bromine, sodium peroxide, persulphates, red lead, and nitrites do not give the reaction (De Koninck, *Zeitsch. anal. Chem.*, **43,** 418).

17. A solution of *tetramethyldiaminodiphenylmethane* in twenty times its quantity of 10 per cent. acetic acid gives a blue coloration with manganese dioxide. The reaction is very sensitive (Trillat. *Chem. Zentralbl.*, 1903, II., 68). The author uses the reaction to detect very small amounts of manganese in plant ash. The substance is ignited with a little alkali hydroxide, and the ash heated with sodium hydroxide and then treated with the reagent and with a little water, acidified with acetic acid; on heating the mixture the blue coloration appears.

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[1] The lead peroxide must first be tested as to its freedom from manganese by evaporating it with sulphuric acid and boiling the residue with nitric acid On this reaction Pichard (*Compt. rend.*, **126**, 550; *Zeitsch. anal. Chem*, **44**, 419) bases a method of detecting manganese in soils, etc. A mixture of 0 5 grm. of the ignited substance, or its ash, with 2 parts of sodium carbonate is fused at not too high a temperature, the resulting mass dissolved in water containing a little nitric acid, the solution added to 0·5 grm. of red lead or brown lead peroxide, and the mixture treated with 4 c.c. of water and 2 c.c of pure nitric acid. On boiling the mixture and allowing it to settle a pink coloration is obtained in the presence of manganous ion.

18. When a manganese compound is treated with *phosphoric acid* and the mixture evaporated to the consistency of syrup, and then more strongly heated (after the addition of a little potassium nitrate if a manganous salt is present) a violet mass (semi-liquid when hot and solid when cold) due to the formation of manganic phosphate, is obtained. The reaction is very sensitive.

19 When any finely powdered manganese compound is fused with 2 to 3 parts of **sodium carbonate** on platinum wire, platinum foil, or the lid of a platinum crucible in the **outer gas or blowpipe flame,** *sodium manganate,* Na_2MnO_4, is formed, and causes the substance to appear *green* while hot and *bluish-green* on cooling, in which process it also becomes opaque. This reaction enables the smallest amount of manganese to be detected. It also succeeds very well with *sodium peroxide* (Hempel).

20. **Borax** and **alkali phosphate** dissolve manganese compounds in the outer oxidising gas flame, forming *transparent violet-red beads,* which on cooling appear *amethyst coloured,* and lose their coloration in the inner flame, owing to the reduction of the manganic compound to a manganous compound The borax glass appears black when a large amount of manganic oxide is present, but the phosphate glass never loses its transparency. It is also more easily discoloured than the borax glass in the inner flame.

21. *Calcium carbonate* shows a buish green fluorescence after contact with a hydrogen flame. But if a trace of a manganese solution is applied to the calcium carbonate, the luminescence will then be deep yellow (Donau, *Monatsh. Chem*, **34,** 919; *Chem. Zentralbl.*, 1913, II., 934).

22 With regard to the *absorption spectra* of manganese compounds of different stages of valency, reference may be made to the communications of W. Jaeschke and J. Meyer (*Zeitsch. phys. Chem.*, **83,** 281, *Chem. Zentralbl.*, 1913, II, 126).

23 For the *microchemical detection* of manganese, see Haushofer, *Mikroskopische Reaktionen,* p 96; Behren Kley, *Mikrochemische Analyse*, 3rd ed., p 88, Schoorl, *Zeitsch. anal Chem.*, **48,** 227, 230; M Wagenaar, *Chem Zentralbl.*, 1912, I., 684.

SEC. 59.

(c) Nickel, Ni, 58·68.

1. *Nickel* is *di-* and *trivalent*, and, in many cases, *tetravalent* in its compounds. *Metallic nickel* in the compact condition is white,

shading into grey, lustrous, hard, and ductible. It has a specific gravity of about 8.8 and melts at about 1452°. It is not oxidised when exposed to the air at the ordinary temperature, but is slowly oxidised on ignition; it is attracted by a magnet, and can itself become magnetic. It is slowly dissolved by hot hydrochloric and dilute sulphuric acids, with the evolution of hydrogen, and is readily soluble in nitric acid. The solutions contain divalent nickel (nickelous ion).

2. *Nickel hydroxide* is pale green, and does not alter on exposure to air. When ignited at a white heat it is converted into amorphous green *nickelous oxide*, NiO (nickel monoxide). Both compounds are soluble in hydrochloric, nitric, and sulphuric acids.

On the other hand, the modification of nickelous oxide which crystallises in octahedra is insoluble in acids, but is rendered soluble by fusion with potassium hydrogen sulphate.

Nickelic oxide, Ni_2O_3 (nickel oxide), which contains trivalent nickel, is black and dissolves in hydrochloric acid, with the liberation of chlorine, to form nickelous chloride. When nickelous hydroxide, or the carbonate or nitrate of divalent nickel, is gently ignited, greyish-green nickelous oxide containing some nickelic oxide is obtained.

3. *The salts of divalent nickel* are usually yellow in the anhydrous condition, and green when hydrated, and produce pale green solutions. They are decolorised on the addition of a certain proportion of a solution of a cobalt salt (3Ni : 1Co). The soluble neutral salts slightly redden litmus (hydrolysis). The salts of volatile acids are, as a rule, readily decomposed on ignition, but nickelous sulphate will stand gentle ignition. Nickelous chloride is insoluble in ether saturated with gaseous hydrogen chloride. (Distinction from cobalt and iron ions.) This affords a means of detecting even small amounts of nickel in the presence of these metals. Aluminium ion, which behaves in the same way as nickel ion, must not be present (Piñerua, *Chem. Zentralbl.*, 1897, I., 1177).

4. **Hydrogen sulphide** does *not* form a precipitate in solutions of the nickelous salts of strong acids in the presence of free acid, but in the absence of free acid a small amount of the nickelous ion separates as black hydrated nickelous sulphide, NiS.

Nickelous acetate solution containing free acetic acid does not give a precipitate, but in the absence of free acid most of the nickel ion is precipitated on continuing the action of the hydrogen sulphide for some time; if, however, the solution contains a sufficient quantity of alkali acetate the dissociation is checked, and the whole of the nickel ion is precipitated, even in the presence of free acetic acid, especially when the liquid is heated during the introduction of the hydrogen sulphide.

Free formic acid and monochloroacetic acid also prevent the precipitation; but if the alkali salts of these acids are present, the precipitation is not prevented from a hot solution, unless a large amount of free acid is present. Gallic acid in an exceedingly dilute sulphuric acid solution also inhibits the precipitation.

5. **Ammonium sulphide** *produces in neutral and alkaline solutions,* and **hydrogen sulphide** *in alkaline solutions, a black precipitate of hydrated nickelous sulphide,* NiS, which is not quite insoluble in ammonium sulphide, especially when free ammonia is present; hence the liquid from which the precipitate has separated usually, and in the presence of ammonia, always shows a brownish coloration,[1] and will then yield a slight precipitate of nickelous sulphide when neutralised with acetic acid and heated. Ammonium chloride, and still more so ammonium acetate, materially promotes the precipitation. Nickel is completely precipitated in the presence of ammonium salts, and in the absence of any considerable quantity of free ammonia, by ammonium sulphide decolorised with sodium sulphite (Lecrenier). Nickelous sulphide is hardly soluble in acetic acid and dissolves with great difficulty in hydrochloric acid. It is almost insoluble in boiling dilute hydrochloric acid, but is readily soluble in hot nitric acid and *aqua regia.*

The separation of nickelous sulphide does not take place immediately, especially in the case of dilute solutions. The presence of ammonia and (in precipitations with hydrogen sulphide water) of acids retards the reaction (Thiel and Ohl, *Zeitsch. anorgan. Chem.*, **61**, 396). These authors regard the brown coloration, which is produced on treating a nickel salt solution with ammonium sulphide in presence of ammonia, as being due to colloidal nickelous sulphide. This is in accordance with the fact that on boiling such brown solutions the nickelous sulphide is precipitated, while the solution is decolorised. The retardation of the reaction in the precipitation of nickelous sulphide is explained by these authors as being due to the polymerisation of a readily soluble into a sparingly soluble sulphide. A similar cause would also account for the striking fact that the precipitation of nickelous sulphide is prevented by relatively weak acids, but that when once precipitated it is only very slightly soluble (oxidation being excluded) in strong acids. According to another view, the explanation of this is that in consequence of the retardation phenomena a false equilibrium is at first established (*cf.* Sec 57, end of 4).

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[1] A similar brown coloration, which may be used for the detection of minute traces of nickelous ion, is obtained when a solution of a nickel salt is treated with tartaric acid and then with sodium hydroxide until alkaline, and is finally saturated with hydrogen sulphide. Under these conditions some of the nickelous ion always remains in solution and gives a brown coloration to the filtrate. Cobalt ion, if not present in very small proportion, is completely precipitated under the same conditions. In the presence of minute quantities, a brown coloration is also obtained, but in such cases the cobaltous sulphide may always be precipitated by means of a large amount of sodium hydroxide (Villiers, *Chem. Zentralbl.*, 1895, I, 117).

6. *Ammonium thioacetate* precipitates nickelous sulphide from ammoniacal solutions of nickel salts *Sodium thiosulphate* does not precipitate nickel ion from acid solutions, and only precipitates it partially and after very long boiling, as nickelous sulphide, from neutral solutions.

7. **Potassium and sodium hydroxide** produce a *pale green precipitate of nickelous hydroxide*, $Ni(OH)_2$, which is insoluble in excess of the precipitant, and does not change on exposure to the air or when boiled (even on the addition of hydrogen peroxide, iodine, or alcohol) After washing it is soluble in ammonium carbonate solution, forming a greenish-blue solution, from which potassium or sodium hydroxide precipitates the nickel ion as an apple-green precipitate of nickelous hydroxide.

8 **Ammonia,** when added in *small* proportion to a solution of a nickelous salt, produces a *slight greenish turbidity;* if added in *greater quantity it readily dissolves the separated compound, forming a blue solution* containing a complex nickel ammonia ion, $Ni(NH_3)^{\cdot\cdot}_4$ or $Ni(NH_3)^{\cdot\cdot}_6$ By adding solid sodium chloride, the chloride of the complex ion may be separated as a violet blue precipitate. Potassium or sodium hydroxide precipitates nickelous hydroxide from' the solution Solutions which contain ammonium salts or free acids are not rendered turbid by the addition of ammonia, owing to the repression of the dissociation of the ammonium hydroxide, *i.e.* formation of complexes.

9. On treating a solution of a nickelous salt with **potassium** or **sodium hydroxide,** adding a sufficient quantity of **bromine water** or a solution of **sodium hypochlorite, potassium ferricyanide** or a **persulphate,** but not hydrogen peroxide or iodine (distinction from cobaltous ion), and heating the liquid, *the whole of the nickel ion is precipitated as black nickelic hydroxide* The precipitate dissolves on the addition of potassium cyanide, forming potassium nickelocyanide (*cf.* 12). The precipitate, after separation from the liquid, is also reduced by a mixture of ammonia and ammonium chloride solutions,

and dissolves as nickelous ammonium hydroxide. The solution takes place somewhat slowly in the cold, but rapidly on heating.

Note on 7 to 9: The presence of non-volatile organic acids and also of sugar prevents or influences the precipitation of the hydroxides of di- and trivalent nickel.

10. **Potassium ferrocyanide** precipitates *nickelous ferrocyanide*, $Ni_2Fe(CN)_6$, from solutions of nickel salts as a greenish-white precipitate, which dissolves with difficulty in hydrochloric acid. (With regard to an analogous reaction with potassium cobaltocyanide, see Sec 60, 12, footnote.)

11. **Potassium ferricyanide** produces a yellowish-brown precipitate of nickelous ferricyanide, $Ni_3[Fe(CN)_6]_2$, which is sparingly soluble in hydrochloric acid. In the presence of ammonium chloride or tartaric acid and a large excess of ammonia, there is obtained a clear brownish-yellow liquid, becoming pale yellow when greatly diluted.

12 **Potassium cyanide** produces a *greenish precipitate of nickelous cyanide*, $Ni(CN)_2$, which dissolves readily in an excess of the precipitant, forming a brownish-yellow solution of potassium nickelocyanide, $K_2Ni(CN)_4$, which does not become darker on exposure to the air Sulphuric and hydrochloric acids re-precipitate nickelous cyanide from this solution (only after some time if it is very dilute), owing to their decomposing the nickelocyanide anion; this new precipitate is only very sparingly soluble in excess of these acids in the cold, but dissolves more easily on boiling. If a current of **chlorine** *is introduced into*, or **bromine** *is added* without heating, to a *solution of potassium nickelocyanide* which has been rendered *alkaline with sodium hydroxide*, and if necessary kept alkaline by the further addition of alkali, *the whole of the nickel gradually separates as a black precipitate of nickelic hydroxide*. (Distinction from cobalt ion.)

Here the complex nickelocyanogen ion is decomposed by the action of the halogen, and the divalent nickel cation is oxidised in alkaline solution into the trivalent condition:

$$Ni(CN)_4K_2+4Br_2=NiBr_2+2KBr+4CNBr—NiBr_2+Br+3NaOH$$
$$=Ni(OH)_3+3NaBr$$

or $$Ni(CN)_4+9Br=Ni^{\cdot\cdot\cdot}+5Br'+4CNBr—Ni^{\cdot\cdot\cdot}+3OH'=Ni(OH)_3$$

Since the halogens also react with cyanogen to form cyanogen halides, the decomposition of the complex nickelocyanogen ion does not take place until there is no longer any cyanogen ion present. Any considerable excess of potassium cyanide is therefore to be avoided (see No. 9, where the converse reaction is in question). *Ammonium sulphide* does not decompose the nickelocyanogen ion, and hence does not precipitate nickelous sulphide from the potassium cyanide solution (Distinction from zinc and manganese ions.)

13. *Potassium thiocarbonate solution*,[1] (K_2CS_3), produces in ammoniacal solutions of nickel salts, if concentrated, a *deep brown-red* coloration, so that the liquid becomes almost opaque and appears nearly black by reflected light. If, however, the nickel solution is extremely dilute the liquid becomes *yellowish-red* on the addition of the reagent (C. D. Braun) The production of this coloration in exceedingly dilute solutions is characteristic of the nickelous ion In the presence of cobalt ion this reaction is completely masked, or nearly so, and in the presence of manganese or zinc ion is more a less masked

14. **Barium carbonate** does *not* precipitate nickelous ion in the cold from aqueous solutions of its salts, with the exception of nickel sulphate It is also *not* precipitated in the presence of *bromine* (Distinction from cobalt ion)

15 **Potassium nitrite** does *not* produce a precipitate even in concentrated solutions of nickel salts to which acetic acid has been added. (Distinction from cobalt ion.) In the case of concentrated solutions of nickel salts which contain alkaline earth ions, or lead ion, yellow crystalline precipitates of nickelous potassium calcium nitrite, etc., may, however, under certain conditions be obtained, these precipitates are only slightly soluble in cold water even in the presence of acetic acid, but dissolve more readily in hot water, forming a green solution (Kunze and O. L. Erdmann). Hence the reaction is only a decisive proof of the presence of cobalt ion (Sec. 60, 75) when ions of the alkaline earths or lead ion are absent

16 *Saturated ammonium molybdate solution* produces in neutral or slightly acid solutions of nickel salts, when heated to about 70° and shaken, a greenish-white crystalline precipitate, which, as a rule, is only formed after some time. (Distinction from cobalt ion.) The reaction is very sensitive and is also suitable for the micro-chemical detection of nickel (Pozzi-Escot, *Chem. Zentralbl.*, 1907, II., 1356).

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[1] To prepare potassium thiocarbonate, K_2CS_3, half of an approximately 5 per cent. solution of potassium hydroxide is saturated with hydrogen sulphide, the other half added, and the whole heated at a moderate temperature with $\frac{1}{25}$th of its volume of carbon bisulphide. The resulting dark red liquid is separated from the undissolved carbon bisulphide and kept in a well-closed flask.

17. *Potassium chromate solution* produces a precipitate in cold neutral solutions of nickel salts, even when concentrated, although only slowly. (Distinction from cobalt ion.) On boiling the liquid, even when very dilute, a chocolate brown *basic chromate*, $NiCrO_4 \cdot 2NiO$, is precipitated; this is soluble in acid and ammonia solution (H. Weil, *Chem. Zentralbl.*, 1911, I., 756).

18. **Dimethylglyoxine** produces in *ammoniacal and acetic acid solutions of nickel salts, even when extremely dilute, a fine red crystalline precipitate.* (Distinction from cobalt, zinc, manganese, iron, and chromium ions.) The reagent is either added in solid form to the strongly ammoniacal solution of the nickel salt, and the liquid heated (Tschugajeff[1]), or the nickelous salt solution is treated with a moderate excess of a 1 per cent. alcoholic solution of the reagent and then rendered just alkaline (Brunck[2]). In this case, only a red coloration is first produced in very dilute solutions, but even then on standing the very characteristic precipitate is formed. Fortini[3] uses the reaction to detect minute quantities of nickel in metal alloys. For this purpose a solution of 0.5 grm. of dimethylglyoxime in 5 c.c. of 98 per cent. alcohol and 5 c.c. of ammonia solution (which reagent may be kept without alteration) is applied to the surface of the substance under examination, which has previously been freed from grease. In the presence of nickel a red coloration is produced (see also Middleton and Miller[4]). F. W. Atack[5] recommends *a benzyldioxime*, which gives a reddish-yellow precipitate, as a still more sensitive reagent.

19. Dicyanodiamidine sulphate (in 10 per cent. aqueous solution) produces in ammoniacal solutions of nickel salts, to which sodium hydroxide has been added, a crystalline yellow precipitate of nickel dicyanodiamidine, $(C_2H_5N_4O)_2Ni + 2H_2O$. As a rule the reaction does not take place immediately, but is *very sensitive and characteristic*. If the reagent is added to a solution of a nickelous salt which has been treated with a little ammonium chloride and ammonia, and the sodium hydroxide then introduced, the blue colour of the solution is immediately changed to yellow, and the precipitation follows after some time (or a long time in the case of dilute solutions) (H. Grossmann and B. Schück, *Chem. Zeit.*, **31**, 535; *Zeitsch. anal. Chem.*, **47**, 168).

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[1] *Ber.*, **38**, 2520; *Zeitsch. anal. Chem.*, **47**, 162.

[2] *Zeitsch. angew. Chem.*, **20**, 834 and 1844; *Zeitsch. anal. Chem.*, **47**, 163.

[3] *Chem. Zentralbl.*, 1913, I., 463.

[4] *Ibid.*, 1916, I., 1072.

[5] *Zeitsch. anal. Chem.*, **53**, 620.

The presence of cane sugar does not influence the reaction (Grossmann and Heilborn, *Ber.*, **41**, 1878).

20. A solution of **Nitroso-β-naphthol** in 50 per cent acetic acid produces a brown precipitate of *nitroso-β-naphthol nickel*, $[C_{10}H_6O(NO)]_2Ni$, in solutions of nickelous salts. The precipitate is decomposed by hydrochloric and sulphuric acid. Hence no precipitate is produced in hydrochloric acid solution (Ilinski and Von Knorre, *Zeitsch. anal. Chem.*, **24**, 595).

21. A solution of 1.2-*Diaminoanthraquinone-3-sulphonic acid* (0·5 grm. in 100 c.c. of concentrated ammonia solution, 310 c.c. of water, and 40 c.c. of 35 per cent. sodium hydroxide solution) produces a blue precipitate in solutions of nickel salts. Traces of ammonia increase the sensitiveness of the reaction, but an excess of ammonia changes the colour to red. (Distinction from cobalt ion.) (Malatesta and Nola, *Chem. Zentralbl.*, 1914, I., 820.)

22. A concentrated solution of *naphthenic acids* in petroleum spirit gives a slight green coloration when shaken with a solution of a nickel salt. No change is produced in the petroleum spirit layer by the addition of hydrogen peroxide. (Distinction from cobalt ion.) (Charitschkoff, *Chem. Zeit.*, **34**, 179.)

23. *Potassium dithio-oxalate* produces a dark red coloration in solutions of nickel salts, even when they are very dilute. The colour is destroyed by acids, sodium hydroxide, and potassium cyanide (H. O. Jones and H. S. Tasker, *Chem. Zentralbl.*, 1910, I., 608).

24. **Borax and alkali phosphate** dissolve nickel compounds in the outer flame forming transparent glasses. The borax glass is violet while hot, and reddish-brown when cold, whilst the alkali phosphate glass is red to brownish-red while hot, but on cooling becomes yellow or reddish-yellow. Small amounts of cobalt mask the coloration. The phosphate glass remains unchanged in the inner flame, but the *borax glass* becomes *grey* and *turbid*, owing to the reduced nickel. On continuing the heating the nickel enters into combination without first melting into one granule, and the glass becomes colourless.

25. When reduced on *charcoal sticks*, as described on p. 88, nickel compounds yield white malleable lustrous metallic particles (separated by powdering the charcoal), which group themselves in the form of a brush upon the point of a magnetised knife. Treated with nitric acid they give a green solution, which may be subjected to further tests.

26. The *halogen compounds* of nickel when introduced on platinum wire into a *Bunsen flame* produce a reddish, very transitory *flame coloration*.

27. For the *micro-chemical detection* of nickel, see Haushofer, *Mikroskopische Reaktionen*, p. 63; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 78; Schoorl, *Zeitsch. anal. Chem.*, **48**, 213; Pozzi-Escot, *Chem. Zentralbl.*, 1907, II., 484 and 1356; 1911, I., 840.

SEC. 60.

(d) Cobalt, Co, 58·97.

1. *Cobalt* is *divalent*, *trivalent*, and, in many cases, *tetravalent* in its compounds. Its specific gravity is about 8·6. Metallic cobalt which has been fused is steel-grey, fairly hard, readily polished, melts with difficulty (melting-point 1489°), and magnetic. It is not oxidised on exposure to the air at the ordinary temperature (pulverulent cobalt obtained by reducing the oxides, *e.g.* in a current of hydrogen, does not scintillate in the air), but is oxidised on ignition. It behaves like nickel towards acids, yielding solutions containing divalent cobalt.

2. *Cobaltous oxide*, CoO (cobalt protoxide), is a light brown, and *cobaltous hydroxide*, $Co(OH)_2$, a pale red powder. Both are easily soluble in hydrochloric, nitric, and sulphuric acids. *Cobaltic oxide*, Co_2O_3 (cobalt sesquioxide), is brownish-black; it is soluble in hydrochloric acid, with the evolution of chlorine, forming cobaltous chloride (protochloride).

3. *Cobaltous salts* containing water of crystallisation are red, whilst the anhydrous salts are usually blue. Their solutions, if not too concentrated, appear pink, the colour being perceptible in very dilute solutions. The soluble neutral salts redden litmus slightly, owing to hydrolysis. As a rule, the salts of volatile acids are readily decomposed on ignition, and only cobaltous sulphate will stand moderate ignition. On evaporating a solution of cobaltous chloride, the red colour changes to blue towards the end of the process, whilst a red solution is again obtained on the addition of water. This change of colour, which also takes place in the case of other cobaltous compounds, is attributed by Ostwald to the cobaltous ion being pink and the undissociated cobaltous salt blue. According to Donnan and Basset the cobalt cation is red; the blue coloration is attributed by these authors to a complex anion, $CoCl'_3$ or $CoCl''_4$.

4. **Hydrogen sulphide** does not produce a precipitate in the

solutions of cobaltous salts, if they contain free acids; when they are neutral a portion of the cobalt is gradually precipitated as black hydrated cobaltous sulphide. Cobaltous acetate is not precipitated to any appreciable extent in the presence of free acetic acid, but in the absence of free acid is precipitated completely or almost completely. But if the solution contains alkali acetate in sufficient quantity, the dissociation of the acetic acid is so checked that, even in the presence of free acid, the whole of the cobalt is precipitated, especially when the liquid is heated during the introduction of the hydrogen sulphide. Free formic acid and monochloroacetic acid also prevent the precipitation. If, however, alkali salts of these acids are present, the precipitation from a hot solution is only prevented when a large quantity of acid is present.

5. **Ammonium sulphide,** *added to neutral and alkaline solutions,* and **hydrogen sulphide** to *alkaline solutions,* precipitates the *whole of the cobaltous ion as black hydrated cobaltous sulphide,* CoS. Ammonium chloride materially promotes the precipitation. Cobaltous sulphide is insoluble in alkali and ammonium sulphide solutions,[1] slightly soluble in acetic acid, and hardly soluble or, if precipitated from a boiling solution, nearly insoluble in hydrochloric acid. Nitric acid and *aqua regia* dissolve cobaltous sulphide on heating. For the explanation of the behaviour of cobaltous sulphide towards acids, reference may be made to what has been said about the analogous behaviour of nickel sulphide (Sec. 59, 5).

6. *Ammonium thioacetate* precipitates cobaltous sulphide from ammoniacal solutions of cobaltous salts. *Sodium thiosulphate* does not produce a precipitate in acid solutions, and only an incomplete one in neutral solutions after very long boiling; the precipitate then formed is cobaltous sulphide.

7. **Potassium** and **sodium hydroxide** produce in solutions of cobaltous salts when sufficiently dilute *precipitates of basic cobaltous salts,* insoluble in excess of the precipitant. *On exposure to the air these become dirty green and subsequently grey-green, owing to the absorption of oxygen;* when boiled (or even on standing in the cold in presence of a sufficient excess of alkali) they are usually transformed into pale red cobaltous hydroxide, containing alkali, and usually showing a doubtful colour owing to the formation of cobaltic hydroxide. If alcohol is added prior to the boiling, the precipitate is rapidly converted into dark brown cobaltic hydroxide. Ammonium chloride, when present in sufficient quantity, prevents the precipita-

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[1] *Cf.*, however, the footnote on p. 231

tion of cobalt by alkali hydroxide. Ammonium carbonate solution completely dissolves the precipitated basic cobaltous salts or cobaltous hydroxide when washed, yielding intense violet-red solutions, in which the addition of a larger quantity of potassium or sodium hydroxide will produce blue precipitates, while the liquids still remain violet.

If, however, an excess of a concentrated solution of potassium hydroxide is added to a solution of a cobaltous salt, or cobaltous hydroxide is heated with a little water and a fragment of sodium hydroxide, the cobaltous hydroxide will dissolve as such, forming a blue solution (Donath, *Zeitsch. anal. Chem.*, **40**, 137). Insoluble cobalt minerals, or metallic cobalt, also give a blue coloration when heated with concentrated alkali solution after roasting.

8 **Ammonia** produces the *same precipitate as potassium hydroxide*, which, however, is soluble (with the exception of a slight green flocculent residue) in an excess of the precipitant, forming a brownish-yellow solution, which becomes brownish-red on exposure to the air through the absorption of oxygen, and from which part of the cobalt ion is precipitated as a blue basic salt on the addition of potassium or sodium hydroxide In the case of solutions which contain *ammonium salts or free acids, no precipitate* is obtained on the addition of ammonia. The ammoniacal solution contains the cobalt in the form of a complex ammonia compound. In this process oxidation is caused by the atmospheric oxygen, so that the cobalt is converted more or less completely into the trivalent form.

9 When a solution of a cobaltous salt is treated with **potassium or sodium hydroxide** and then with **bromine water, sodium hypochlorite solution, a persulphate, hydrogen peroxide, barium peroxide or iodine,** or when a sufficiently dilute cobaltous salt solution is boiled with **sodium peroxide,** *the whole of the cobalt separates as brownish-black cobaltic hydroxide* This precipitate does *not re-dissolve* either in a mixture of ammonia and ammonium chloride solutions, or in potassium cyanide solution. If, however, a considerable quantity of nickelic hydroxide is also present, the potassium cyanide solution dissolves the cobaltic hydroxide as well as the nickelic hydroxide. The above-mentioned oxidising agents (with the exception of sodium peroxide) do not produce a precipitate in ammoniacal solutions.

If a solution of a cobaltous salt is treated with *sodium hydrogen carbonate* in excess, and then with *hydrogen peroxide*, a green solution is obtained, which contains a compound of trivalent cobalt not yet isolated (method of detecting cobalt ion in presence of nickel ion, Durrant, *Chem. News*, 72, 228; *Chem. Zentralbl.*, 1896, II., 634). For this purpose Jaworowsky (*Chem. Zentralbl.*, 1898, I., 144) recommends a method in which the solution of the cobaltous salt is neutralised with sodium carbonate, then treated with crystalline *sodium pyrophosphate* until the precipitate first formed is re-dissolved, the liquid filtered from the undissolved pyrophosphate, and the filtrate treated with sodium carbonate and bromine water, an excess of the latter being avoided.

Notes to 7–9: The presence of non-volatile organic acids or of sugar influences or prevents the precipitation of cobalt as hydroxide in di- or trivalent form, owing to the formation of complex anions.[1] In like manner, glycerin forms a complex anion with cobalt, so that alkali hydroxides do not produce a precipitate in such solutions, but only a deep blue coloration. This becomes green through oxidation on exposure to the air, and more rapidly on the addition of hydrogen peroxide. If a solution of a cobaltous salt to which glycerin has been added is covered with a few drops of ammonia solution, the ammoniacal layer becomes intense lemon-yellow in colour. (Distinction from nickel ion.) (Ditz, *Chem. Zeit.*, 25, 109.)

10. **Potassium ferrocyanide** produces in cobalt solutions a green precipitate of *cobaltous ferrocyanide*, $Co_2Fe(CN)_6$, which dissolves with difficulty in hydrochloric acid.

11. **Potassium ferricyanide** produces a brownish-red precipitate of *cobaltous ferricyanide*, $Co_3[Fe(CN)_6]_2$, which is only very slightly soluble in hydrochloric acid. If the solution of the cobaltous salt is treated with tartaric acid or ammonium chloride and then with ammonia in excess, *so that a clear strongly ammoniacal solution* is obtained, and potassium ferricyanide then added, a dark yellowish-red liquid is produced in the case of concentrated solutions, and the coloration may still be recognised even in great dilution (Skey-Gintl). This is a very sensitive reaction, and is particularly suitable for the detection of cobalt ion in the presence of nickel ion.

12. On adding **potassium cyanide** to a cobaltous salt solution a brownish-white precipitate of *cobaltous cyanide* (cobalt protocyanide), $Co(CN)_2$, is produced; this is readily soluble in excess of potassium cyanide solution, the complex anion of *potassium cobaltocyanide* being formed.[2] Acids precipitate cobaltous cyanide, $Co(CN)_2$, from

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[1] *Vide infra*, 19.

[2] If the precipitation with potassium cyanide is made with complete exclusion of air (in a solution of thoroughly boiled water or by means of the

this solution *If, however, the solution is boiled with excess of potassium cyanide and in the presence of free hydrocyanic acid* (liberated by the addition of one or two drops of hydrochloric acid), then treated with potassium or sodium hydroxide, and a current of chlorine conducted into it, without heating, or bromine water is added, the anion *potassium cobalticyanide*, $K_3Co(CN)_6$, is formed, and the solution of this salt does not give a precipitate with acids. (Important distinction from nickel ion) If *potassium nitrite* and *acetic acid* are added to the still unaltered solutions of potassium cobaltocyanide, the liquid assumes a blood-red, or if very dilute, only a pink colour, owing to the formation of ions of a potassium cobalt nitrocyanide, $K_4Co_2(CN)_9NO_2,3H_2O$ On shaking a solution of potassium cobaltocyanide with sodium hydroxide, it absorbs oxygen and becomes brown (C D Braun), and when treated with yellow ammonium sulphide it becomes blood-red (Tattersall and Papasogli) The latter reactions sharply distinguish cobalt ion from nickel ion

13 **Potassium thiocarbonate solution** (*cf* Sec 59, 13) gives a *deep brown to black coloration* with concentrated solutions of cobaltous salts and a *yellowish coloration* with very dilute solutions.

14 **Barium carbonate** behaves towards solutions of cobaltous salts in the same way as towards solutions of nickelous salts Black cobaltic hydroxide, however, is precipitated by barium carbonate after the addition of bromine (Distinction from nickel ion)

15 On adding **potassium nitrite** in not too large excess to a neutral or slightly acid solution of a cobaltous salt, then **acetic acid** until the reaction is strongly acid, and allowing the mixture to stand in a moderately warm place, *the whole of the cobalt ion separates* (very rapidly from concentrated solution and after some time from dilute solutions) *in the form of a bright yellow crystalline precipitate of potassium cobaltinitrite*, $2K_3[Co(NO_2)_6]+3H_2O$ (Fischer's salt) (Fischer-Stromeyer). The precipitate dissolves to a considerable extent in pure water, but is only slightly soluble in concentrated solutions of potassium salts and in alcohol, and is insoluble in the presence of potassium nitrite When boiled with water it dissolves to a small extent, forming a red solution, which remains clear when cold and from which alkalis precipitate cobaltous hydroxide. This is a particularly good reaction, and is well suited for the distinction and

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introduction of sulphur dioxide) the precipitate will be intense red. Its solution in excess of potassium cyanide solution gives an orange-red precipitate with a solution of zinc sulphate containing sulphur dioxide, a yellow precipitate with nickel sulphate solution, and a red precipitate with cobaltous sulphate solution (E Pinerua Alvarez, *Chem. Zeit.*, 1910, R, 189).

separation of nickel ion from cobalt ion. It should be noted that it is advisable to use as small a volume of liquid as possible, *i.e.* to use *concentrated* solutions and reagents (*cf*, however, Sec. 59, 15).

16. **Potassium thiocyanate** in concentrated solution forms a *deep blue liquid* (which solidifies in crystalline form) with concentrated solutions of cobaltous salts. Cobaltous thiocyanate is readily soluble in alcohol (Schönn, *Zeitsch anal. Chem* , **9**, 210). The reaction also takes place in dilute solutions, when the liquid is shaken with ether-alcohol or, better, a mixture of ether and amyl-alcohol (Vogel, *Ber.*, **12**, 2311) ; the layer of ether and alcohol is then coloured blue (N. Rusting, *Chem Zentral.*, 1899, I., 709). (Concentrated solutions of nickel salts free from cobalt ion impart a greenish coloration to the amyl-alcohol) Ferric ion interferes with the reaction, but may be removed by shaking its thiocyanate with ether alone, or reduced to a colourless condition by adding solid thiosulphate to the solution after treatment with potassium thiocyanate, filtering the liquid, and shaking the filtrate with ether alcohol (Wefers-Bettink, *Chem. Zentralbl.*, 1899, I., 904). The disturbing influence of ferric ion may also be eliminated by the addition of sodium carbonate solution, which decomposes ferric thiocyanate, but does not attack cobaltous thiocyanate, or by the addition of potassium sodium tartrate solution, which prevents the iron from reacting (Vogel, *loc. cit.*; Treadwell, *Zeitsch. anorgan. Chem* , **26**, 108).

17. *Potassium chromate solution* produces in neutral solutions of cobalt salts, even in the cold (on boiling in the case of very dilute solutions), a brownish-red precipitate of $CoCrO_4.CoO.H_2O$, which is soluble in acids and in ammonia solution. This is a very sensitive reaction (H. Weil, *Chem Zentralbl.*, 1911, I , 756).

18. **Nitroso-β-naphthol** *produces a voluminous purple-red precipitate of cobalti-nitroso-β-naphthol*, $[C_{10}H_6O(NO)]_3Co$, in solutions of cobaltous salts. The solution to be tested for cobalt is acidified with hydrochloric acid, treated with an equal volume of alcohol, and warmed. A *freshly prepared* solution of α-nitroso-β-naphthol in 50 per cent. acetic acid is then added in sufficient excess (in order to insure the oxidation of the cobalt ion into the trivalent condition), and the liquid heated to boiling point. In the presence of cobalt ion the fine purple-red precipitate is immediately produced; but if only traces are present the compound remains in solution, and only a red coloration is produced. In this case, however, even when the solution is extremely dilute, a precipitate may still be obtained when the acidified solution to be tested for cobalt ion is treated with an

aqueous solution of α-nitroso-β-naphthol, and then heated. The solution obtained by treating α-nitroso-β-naphthol contains only 1 part in 5000 parts. Hence, an aqueous solution cannot be used for the separation of any considerable quantity of cobalt ion. This is a very sensitive and characteristic reaction, which, applied in this manner cannot lead to any mistake. (Distinction from nickel ion.) (M. Ilinski, *Chem. Zeit.*, 19, 1121.) The red cobaltic compound is exceedingly stable towards acids, alkalis, and oxidising and reducing agents. When heated with ammonium sulphide, however, it yields cobaltous sulphide (Ilinski and von Knorre, *Zeitsch. anal. Chem.*, **24**, 595).

F. W. Atack[1] renders the reaction particularly sensitive. He dissolves 0.1 grm. of α-nitroso-β-naphthol in 20 c.c. of boiling water, to which 1 c.c. of dilute sodium hydroxide solution is added, filters the liquid and dilutes the filtrate to 200 c.c. By means of this stable reagent as little as 0.001 mgrm. of cobalt in 1 c.c. of water may be detected. The neutral or slightly alkaline solution is treated with 1 c.c. of ammonium chloride solution and 1 c.c. of the reagent; a stable red coloration is produced, even after acidification with sulphuric acid, in the presence of cobalt ion.

19. **Dimethylglyoxime** does *not* produce a precipitate in ammoniacal solutions of cobaltous salts. (Distinction from nickel ion.) The solution containing the dimethylglyoxime and cobalt salt becomes wine-red on the addition of hydrogen sulphide or alkali sulphide (Kraut; *Zeitsch. angew. Chem.*, 19, 1793).

20. *Dicyanodiamidine sulphate* does *not* produce a precipitate in ammoniacal solutions of cobalt salts on the addition of sodium hydroxide. (Distinction from nickel ion.) The addition of a sufficient quantity of cane sugar to the solution beforehand prevents any possibility of the separation of cobaltous hydroxide. This is due to the formation of a complex ion. The latter produces an intense red coloration, which may also be used for the detection of minute quantities of cobalt ion in the presence of a large amount of nickel ion since it may be seen very distinctly after the precipitation of the latter with dicyanodiamidine sulphate (Grossmann and Heilborn, *Ber.*, **41**, 1878; *Chem. Zentralbl.*, 1908, II., 199 and 1909, II., 932).

21. *Diamino-anthraquinone sulphonic acid* (see Sec. 59, 21) produces a blue precipitate or blue coloration in solutions of cobalt salts. The addition of ammonia increases the sensitiveness and does not change the colour. (Distinction from nickel ion.) Ammonium chloride also produces no alteration in the colour. (Distinction

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[1] *Chem. Zentralbl.*, 1915, II., 491.

from copper ion.) (Malatesta and Nola, *Chem. Zentralbl.*, 1914, I., 820.)

22. *A solution of naphthenic acids* in petroleum spirit becomes red when shaken with a solution of a cobaltous salt. On adding hydrogen peroxide to the petroleum spirit solution, the colour of the latter changes to greenish-brown (Charitschkoff, *Chem. Zeit.*, **34**, 479).

23. *Potassium dithio-oxalate* produces in solutions of cobalt salts, even when very dilute, a dark reddish-brown coloration, which is much more stable towards acids and potassium cyanide than the corresponding nickel coloration, so that it affords a means of detecting cobalt ion in the presence of nickel ion (H. O. Jones and H. S. Tasker, *Chem. Zentralbl.*, 1910, I., 608).

24. **Borax** *dissolves cobalt compounds in the inner and outer flame, forming transparent bright blue* (violet by candlelight) *glasses*. This reaction is both characteristic and sensitive.

25. When reduced on *charcoal sticks*, as described on p. 88, cobalt compounds show a similar behaviour to that of nickel compounds. The resulting solution is red.

26. For the *microchemical detection* of cobalt, see Haushofer *Mikroskopische Reaktionen*, p. 63; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 75; Schoorl, *Zeitsch. anal. Chem.*, **48**, 211; Richter, *Chem. Zentralbl.*, 1901, I., 1310; Pozzi-Escot, *Chem. Zentralbl.*, 1907, II., 484; 1909, II., 656; 1911, I., 840.

SEC. 61.

(e) **Iron,** Fe, 55·84.

(*a*) **Ferrous ion,** Fe··.

1. *Iron* is present in its compounds in the *divalent* (ferrous salts), *trivalent* (ferric salts), and *hexavalent* (ferrates) condition. The latter compounds, in which the iron is present in the anion FeO''_4, are not very stable. On the other hand, the two series of compounds of divalent and trivalent iron are important. They differ in very many of their reactions. Divalent iron is converted by oxidising agents into trivalent iron. Reducing agents cause ferrous compounds, *i.e.* those of divalent iron, to be formed from ferric compounds.

Metallic iron in the pure condition is whitish-grey, has a specific gravity of about 7·8, and is lustrous, hard, and ductile, is very difficult to melt (melting-point about 1550°), and is attracted by a magnet. (The metals described in everyday life by the collective name of "iron" invariably contain carbon, sometimes chemically combined as carbide (Fe_3C, cementite), and sometimes also in the free condition as graphite Their colour is more or less grey They also invariably contain other elements, some of which, even in small quantities, have a considerable influence on the physical properties) When exposed to the action of air and moisture iron becomes covered with a layer of rust (ferric hydroxide), and upon ignition in the air it becomes coated with black ferrous ferric hydroxide.

Hydrochloric and dilute sulphuric acids dissolve iron with the evolution of hydrogen. If the iron contains carbide the hydrogen will contain hydrocarbons These solutions contain ferrous ion, $Fe^{\cdot\cdot}$. Dilute nitric acid dissolves iron to an extent depending upon the degree of dilution and the temperature, either without the evolution of gas but with the formation of ammonia ion while ferrous nitrate, $Fe(NO_3)_2$, is produced, or with the simultaneous evolution of nitrous and nitric oxides and production of ferric nitrate, $Fe(NO_3)_3$ In the case of iron containing carbide some carbon dioxide is also evolved, whilst when graphite is present it will remain undissolved, together with a humus like substance, which is soluble in alkali solutions

2 *Ferrous oxide*, FeO (iron protoxide), is black, whilst its hydroxide, $Fe(OH)_2$, is white, but in the moist condition the latter absorbs oxygen and rapidly becomes grey-green and finally brownish-red Both oxide and hydroxide are readily soluble in hydrochloric, sulphuric, and nitric acids

3 *The salts of divalent iron* (ferrous salts) when anhydrous are white, but when containing water of crystallisation have a greenish colour, their solutions only appear green when in the concentrated condition When exposed to the air they absorb oxygen, and are converted more or less completely into soluble ferric salts, whilst there is some precipitation of basic ferric salts, *e g* $2FeSO_4+O = Fe_2O(SO_4)_2$ Chlorine, bromine hydrogen peroxide or nitric acid at the boiling temperature oxidise ferrous salts in solution rapidly and completely to ferric salts. In the oxidation with nitric acid nitric oxide is also formed from the acid, and gives a brown colour to the ferrous salt solution, in which it dissolves (see Sec 130, 6). The dark brown coloration of the solution produced is transitory (see 12) The soluble ferrous salts do *not* redden litmus (but this is *only* the case when they are quite pure and *absolutely free from ferric salts*). The ferrous salts of volatile acids are decomposed on ignition.

4. **Hydrogen sulphide** does *not* produce a precipitate in solutions of ferrous salts when strongly acidified, and in neutral or slightly acid solutions produces either no precipitate at all or an incomplete black precipitate of ferrous sulphide. Solutions which have been treated with sodium acetate and a little free acetic acid yield only an incomplete precipitate, even on heating, the amount of the precipitate depending upon the extent to which the sodium acetate preponderates and represses the dissociation of the acetic acid The addition of monochloroacetic acid or of formic acid in sufficient quantity also prevents the precipitation, even when alkali salts of these acids are present.

5. **Ammonium sulphide** precipitates from *neutral and alkaline*, and **hydrogen sulphide** from *alkaline, solutions the whole of the iron as a black hydrated precipitate of ferrous sulphide*, FeS, which is insoluble in alkali hydroxide and alkali sulphide solutions, but readily soluble in hydrochloric and nitric acids, and when exposed to the air becomes reddish-brown, owing to its oxidation to basic ferric sulphate. Extremely dilute solutions of ferrous salts at first become green on the addition of ammonium sulphide, owing to the formation of colloidal ferrous sulphide, and only after standing for a considerable time in a warm place does the ferrous sulphide separate as a black precipitate. The presence of ammonium chloride materially promotes the precipitation. According to Stokes ammonium polysulphide produces a precipitate of ferric sulphide, Fe_2S_3 (*Chem. Zentralbl*, 1907, I., 1663).

6. *Ammonium thioacetate* does not produce a precipitate in acid solutions of ferrous salts, but precipitates ferrous sulphide from *alkaline solutions*. *Sodium thiosulphate* does not give a precipitate.

7. **Potassium or sodium hydroxide,** and also **ammonia,** give a precipitate of *ferrous hydroxide*, $Fe(OH)_2$, which at the moment of precipitation appears white, but in a very short time becomes *dirty green* and finally *reddish-brown*, owing to absorption of oxygen from the air. The precipitation by potassium or sodium hydroxide is partially, and that by ammonia entirely, prevented by the presence of ammonium salts Such alkaline solutions containing ammonium salts yield precipitates of ferrous ferric hydroxide and ferric hydroxide when left exposed to the air. On adding *hydroxylamine* to a solution of a ferrous salt complete precipitation of the ferrous ion as ferric hydroxide takes place, even in the presence of ammonium salts, owing to an oxidation process (Ebler, *Zeitsch. anal Chem* , **47**, 671)

Non-volatile organic acids, sugar, etc., prevent or influence the precipitation of ferrous salts by alkali hydroxides or ammonia.

8. **Potassium cyanide** produces a red-brown precipitate of *ferrous cyanide*, $Fe(CN)_2$. This dissolves in *excess* of potassium cyanide solution in the form of *potassium ferrocyanide*, $K_4Fe(CN)_6$. Since the whole of the iron in this compound is present as complex anion, $Fe(CN)''''_6$, it no longer shows the reactions of ferrous ion, and is therefore not reprecipitated as ferrocyanide on the addition of acid.

9. **Potassium ferricyanide** *produces in solutions of ferrous salts a bluish-white precipitate of ferrous potassium ferrocyanide*, $K_2Fe_3[Fe(CN)_6]_2$, which soon becomes blue through absorption of oxygen from the air. Nitric acid or chlorine converts it immediately into Prussian blue (ferric ferrocyanide), $3K_2Fe_3[Fe(CN)_6]_2 + 9Cl = 6KCl + FeCl_3 + 2Fe_4[Fe(CN)_6]_3$. The precipitate is also produced in a solution which has been treated with tartaric acid.

10. **Potassium ferricyanide** *produces a fine blue precipitate of ferrous ferricyanide* (Turnbull's blue), $Fe_3[Fe(CN)_6]_2$. This does not differ in colour from true Prussian blue. It is insoluble in hydrochloric acid, but is readily decomposed by alkali hydroxide. When the iron solution is very dilute the reagent produces only a dark bluish-green coloration.

11. **Potassium thiocyanate** has no effect whatever upon solutions of ferrous salts *not containing ferric ion.*

12. On treating a ferrous salt solution with excess of concentrated *sulphuric acid* and dropping a **crystal of potassium nitrate** into the solution, brownish-red streaks proceeding from the crystal will soon appear (solution of nitric oxide in ferrous salt). See also the reaction of nitrate ion, Sec. 130, 6. (Method of detecting ferrous salt in presence of ferric salt. Blum, *Zeitsch. anal. Chem.*, **44**, 10.)

13. An aqueous solution of *α-nitroso-β-naphthol* produces in dilute neutral solutions of ferrous salts a green coloration, whilst on standing a slight flocculent green precipitate of *ferrous nitroso-β-naphthol* separates. Free mineral acids (*i.e.* hydrogen ions) prevent the formation of the compound, which is therefore also not produced in concentrated ferrous sulphate solution containing ferric sulphate (*i.e.* hydrolytically dissociated). But if sodium acetate is added the precipitate is formed. On adding an excess of α-nitroso-β-naphthol in acetic acid solution to ferrous salt solutions there is produced a greenish-black precipitate, a mixture of the ferrous and ferric salt, which on standing is completely converted into the ferric compound (Sec. 62, 13).

14. A solution of *naphthenic acid* in petroleum spirit, when shaken with a neutral or slightly acid solution of a ferrous salt, extracts the whole of the ferrous salt, which imparts an intense chocolate-brown coloration to the petroleum spirit layer. (Distinction from ferric ion.) (Charitschkoff, *Chem. Zeit.*, **35**, 163.)

15. On treating a solution of a ferrous salt with a few drops of *phosphotungstic acid reagent* (2 grms sodium phosphotungstate, 5 c.c. hydrochloric acid, and 250 c.c. of water), and adding sodium hydroxide solution, an intense sky-blue coloration is produced. (Distinction from ferric compounds.) This is a very sensitive reaction (Richaud & Bidot, *Chem. Zentralbl.*, 1909, I., 1196). Other reducing agents give the same reaction, which is thus not a specific ferrous ion reaction (Popesco, *Chem. Zentralbl.*, 1916, II., 127).

16. When a solution of a ferrous salt is treated with tartaric acid, a little alcoholic *dimethylglyoxime* solution added, and then an excess of ammonia, an intense red coloration is produced, which fades on exposure to the air, owing to the oxidation of the ferrous complex. Ferric compounds do not give this reaction, which is a very sensitive one (Slawik, *Chem. Zeit.*, **36**, 51; Tschugajeff and Orelkin, *Zeitsch. anorgan. Chem.*, **89**, 401; *Zeitsch. anal. Chem.*, **54**, 376).

17. *Protocatechuic acid* does *not* affect acid solutions of ferrous salts. (Distinction from ferric compounds.) In *slightly* alkaline solution, even when very dilute, it produces a *red* coloration, which is destroyed by excess of hydroxyl ions. It is, therefore, best to treat the slightly acid solution of the ferrous salt with the reagent, and then to add sodium carbonate solution, an excess of which has no injurious effect. If other cations are present which form coloured precipitates, the liquid should be filtered to make the coloration more distinct. Substances which have a disturbing influence on other reactions of iron ions in alkaline solution do not affect this colour reaction (O. Lutz, *Chem. Zeit.*, **31**, 570).

18. **Barium carbonate** does *not* produce a precipitate in the cold in aqueous solutions of ferrous salts, with the exception of ferrous sulphate.

19. **Borax** dissolves ferrous compounds in the oxidising flame, forming *yellow to dark red* glasses. On cooling, they appear colourless to dark yellow. In the inner flame the beads become bottle-green, owing to the reduction of the trivalent iron which has been formed, into divalent iron. **Alkali phosphate** behaves in a similar manner, but the colour of its glass fades to a more pronounced extent on cooling, and the reduction phenomena are less distinct.

20. When reduced on *charcoal sticks* (p. 88), ferrous compounds yield a dull black powder which is attracted by a magnet. The reduced iron yields, when dissolved in a few drops of *aqua regia*, a yellow solution, to which the tests described in Sec. 62 may be applied.

21. With regard to the *microchemical detection* of ferrous compounds, see Haushofer, *Mikroskopische Reaktionen*, p. 48.

SEC. 62.

(β) **Ferric ion**, $Fe^{\cdots}$.

1. As met with in nature, crystalline *ferric oxide*, Fe_2O_3 (iron oxide), is steel grey. When ground up it yields a brownish-red powder, as does also ironstone and all artificially prepared ferric oxides.

Ferric hydroxide is more reddish-brown. Both are soluble in hydrochloric, nitric, and sulphuric acids—the hydroxide readily, and the oxide with more difficulty and only completely after heating for a long time. Reducing agents on the one hand, and manganese dioxide on the other, greatly promote the solution. Ferric oxide dissolves with comparative ease in hydrofluoric acid (Deussen, *Zeitsch. angew. Chem.*, **18**, 813). When heated in a current of dry hydrogen chloride, ferric hydroxide is converted into chloride, which volatilises. Part of the iron remains behind as ferrous chloride, but if the hydrogen chloride contains some chlorine the volatilisation is complete. (Method of separation from aluminium (Gooch and Havens, *Chem. Zentralbl.*, 1899, 1., 1270), and from chromium, zirconium, and beryllium (Havens and Way, *Zeitsch. anorgan. Chem.*, 21, 389).) Ferrous ferric oxide, Fe_3O_4, is black; it dissolves in hydrochloric acid as ferrous and ferric ions, and in *aqua regia* as ferric ion.

2. The neutral anhydrous *ferric salts* are nearly white; the basic salts are *yellow or reddish-brown*. The colour of the solutions is brownish-yellow and becomes reddish-yellow when heated. The soluble neutral salts *redden litmus*, owing to hydrolysis. The ferric salts of volatile acids are decomposed when heated.

Ferric chloride is much more soluble in *ether* in the presence of hydrochloric acid than in water, so that it can be extracted by shaking its aqueous solution with ether (saturated with hydrochloric acid). This affords a means of separating iron ion from the ions of many other metals (aluminium, chromium, manganese, cobalt, nickel, uranium, copper, vanadium), and incompletely from titanium, zinc, calcium, magnesium, potassium, and sodium.

3. **Hydrogen sulphide** produces in solutions acidified with strong acids, especially on heating, *a milky-white turbidity of liberated sulphur*, the ferric ion being meanwhile reduced to ferrous ion:

$$2Fe^{\cdot\cdot\cdot}+H_2S=2Fe^{\cdot\cdot}+2H^{\cdot}+S$$

for example

$$Fe_2(SO_4)_3+H_2S=2FeSO_4+H_2SO_4+S$$

On the rapid addition of hydrogen sulphide water to neutral solutions there is produced, in addition to the separation of sulphur, a transitory blue-black coloration (presumably due to the momentary formation of ferrous sulphide). Hydrogen sulphide precipitates most of the ferric ion from a neutral solution of ferric acetate, but if a sufficient quantity of free acetic acid is present only sulphur separates. A solution of a ferric salt containing sodium acetate and a large amount of free acetic acid yields, on treatment with hydrogen sulphide in the cold, practically nothing but separated sulphur, but on heating the liquid part of the ferric ion is precipitated as ferrous sulphide. Monochloroacetic acid, and also formic acid, when added in sufficient quantity, prevents the precipitation even when alkali salts of these acids are present and the liquid is heated.

4. **Ammonium sulphide** precipitates from *neutral and alkaline solutions*, and **hydrogen sulphide** from *alkaline solutions, the whole of the ferric ion as black hydrated iron sulphide.* In many cases this is invariably *ferric sulphide*, Fe_2S_3, as *e.g.* when a neutral solution of a ferric salt is dropped into excess of a solution of yellow ammonium sulphide (Berzelius). According to the experiments of Stokes upon the interaction of precipitated iron sulphide and zinc hydroxide (*Chem. Zentralbl.*, 1907, I., 1663), *ferric sulphide* is always precipitated from alkaline solutions. In other cases, *e.g.* in presence of a neutral salt of trivalent iron, the aqueous solution of which undergoes hydrolytic dissociation, the precipitate is a mixture of *ferrous sulphide and sulphur*, since under these conditions there is first reduction with the separation of sulphur, and then precipitation:

$$2Fe^{\cdot\cdot\cdot}+3(NH_4)_2S=2FeS+S+6NH_4$$

for example

$$2FeCl_3+3(NH_4)_2S=2FeS+S+6NH_4Cl$$

In the case of very dilute solutions the reagent at first produces only a blackish-green coloration in the liquid. The colloidal ferrous sulphide only separates as a precipitate after standing for a long time. Ammonium chloride has a pronounced influence in promoting the separation. The solubility characteristics of ferrous sulphide have been given in the section on ferrous ion (Sec. 61, 5).

5 *Ammonium thioacetate* causes immediate reduction to ferrous ion in acid solutions of ferric salts; it precipitates ferrous sulphide from alkaline solutions. *Sodium thiosulphate* gives a violet coloration with solutions of ferric salts, and reduces the iron to the divalent condition, but does not form a precipitate.

6. **Potassium** and **sodium hydroxides** (also *alkali peroxides*) and **ammonia** produce a *voluminous reddish-brown precipitate of ferric hydroxide*, $Fe(OH)_3$ (containing alkali), which is insoluble in excess of the precipitant and in solutions of ammonium salts. Non-volatile organic acids or sugar, when present in sufficient quantity, entirely prevent the precipitation, owing to the formation or complex anions (*cf.* Roszkowski, *Zeitsch. anorgan, Chem.*, **14**, 1, *Zeitsch. anal. Chem*, **37**, 111)

Zinc oxide and *mercury oxide* precipitate trivalent iron as hydroxide in the same way as the alkalis.

7 **Potassium cyanide** produces a reddish-brown precipitate of *ferric cyanide*, $Fe(CN)_3$, in solutions of ferric salts The precipitate dissolves in excess of potassium cyanide solution, forming the ions of potassium ferricyanide, $K_3Fe(CN)_6$.

8 **Potassium ferrocyanide** produces, *even in dilute solutions a fine blue precipitate of ferric ferrocyanide* (*Prussian blue*) $Fe_4[Fe(CN)_6]_3$:

$$4FeCl_3+3K_4Fe(CN)_6=Fe_4[Fe(CN)_6]_3+12KCl$$

This is only slightly soluble in hydrochloric acid, but is decomposed by potassium hydroxide, with the separation of ferric hydroxide. Prussian blue is somewhat soluble in excess of potassium ferrocyanide solution.

Minute traces of ferric ion cannot be detected by means of potassium ferrocyanide in solutions containing a large amount of hydrochloric acid or in neutral solutions containing much ammonium chloride In the case of solutions containing ammonium chloride the reaction is only produced after the addition of hydrochloric acid (Vulpius). Ammoniacal solutions of ferric salts which have been treated with tartaric acid do not give a precipitate with potassium ferrocyanide. (Distinction from manganous ion. L. Blum)

9. **Potassium ferricyanide** gives a *dark reddish-brown coloration*, but *no precipitate*, with solutions of ferric salts.

10. **Potassium thiocyanate,** when added in not too small a

quantity to *acid solutions of ferric salts*, produces an *intense blood-red coloration*, owing to the formation of ferric thiocyanate, $Fe(CNS)_3$, or of soluble ferric potassium thiocyanate (Kruss and Moraht). This colour disappears on adding a little alcohol and heating the liquid.

In the case of solutions of ferric salts which have been treated with sodium acetate, and so coloured more or less red by the resulting ferric acetate complex compound, the blood-red coloration of ferric thiocyanate only appears after the addition of a large amount of hydrochloric acid. This is also the case when the solution contains oxalic, tartaric, citric, malic, iodic, phosphoric, arsenic, or hydrofluoric acids. The presence of mercuric compounds influence or prevent the occurrence of the reaction In the presence of *nitric acid* the reaction must be carried out in the *cold*, because hot nitric acid decomposes thiocyanogen compounds by oxidation; if the oxidation is not complete the *nitrite ion* formed may *itself give a red coloration*, so that, on the one hand, there may be no reaction when ferric ion is present, whilst, on the other hand, under certain conditions a red coloration may appear when it is absent. By means of potassium thiocyanate ferric ion may be detected in solutions which are so dilute that no other reagent produces a perceptible reaction with them. In such cases the red coloration produced may be recognised most distinctly when the test-tube is placed on white paper and viewed from above The sensitiveness of the reaction may be still further increased by treating the solution containing the ferric compound with hydrochloric acid, and then with an excess of a solution of potassium thiocyanate, freshly prepared from the crystals, and shaking it gently with a little *ether*. The ferric thiocyanate dissolves in the ether, and the ethereal layer is then more or less red in colour.

11 **Barium carbonate** *precipitates, even in the cold, the whole of the ferric ion as ferric hydroxide* mixed with basic salt. (*Method of separating the ions of trivalent iron from the divalent ions of the fourth group.*)

Analogous precipitations of basic ferric salts (and effecting the same separations) may be produced by treating suitably dilute solutions, containing ammonium chloride, in the cold with *ammonium carbonate until a permanent precipitate is nearly formed* (which might contain carbonates of the divalent metals), and then precipitating the ferric hydroxide mixed with basic ferric salt; or by treating the neutral or still slightly acid solution with a certain excess of *alkali acetate* or *formate* and then boiling it. In all these cases hydrolytic dissociation of the neutral ferric salt occurs. On heating the liquid the ferric hydroxide then present in colloidal solution is precipitated.

12. On adding a small quantity of a solution containing ferric ion to the blue liquid obtained by treating *fuming hydrochloric acid* with a little *cobaltous chloride* or *nitrate*, the blue colour of the solution changes to *green*. The reaction is particularly suitable for the detection of ferric ion in acids or in the presence of ferrous ion (Venable).

13. A solution of *α-nitroso-β-naphthol* in dilute (about 50 per cent.) acetic acid produces in neutral or slightly acid solutions of ferric salts a *voluminous brownish-black precipitate* of *ferric nitroso-β-naphthol*, $(C_{10}H_6O.NO)_3Fe$. (Distinction from many metals, but not from cobalt and copper. Ilinski and von Knorre, *Ber.*, **18**, 2788.)

14. *Protocatechuic acid solution* produces in slightly acid solutions of ferric salts a *bluish-green* coloration, and in *slightly alkaline* solutions a *red* coloration. The coloration is destroyed by excess of acid and alkali hydroxide (but not by alkali carbonate). On adding a few drops of the reagent to an acid solution of trivalent iron, and then an excess of sodium carbonate, a red coloration is obtained, even when the solution is diluted to 1 : 10,000,000 (O. Lutz, *Chem. Zeit.*, **31**, 570).

15. A solution of *diphenylcarbazide* in petroleum spirit produces, when shaken with a ferric salt solution, a peach-red coloration (Cazeneuve, *Zeitsch. anal. Chem.*, **41**, 568).

16. *Potassium molybdenum cyanide* gives an *intense blue coloration* with solutions of ferric salts, even when very dilute. The reagent is prepared by mixing 1 part of potassium molybdenum chloride, K_3MoCl_6, with 2 parts of potassium cyanide, gradually adding 6 parts of water, and heating the whole to boiling point.

17. Ferric salts behave in the same way as ferrous compounds when fused into **borax or alkali phosphate beads,** or heated on *charcoal sticks* (p. 88).

18. With regard to the *microchemical detection* of trivalent iron see Haushofer, *Mikroskopische Reaktionen*, p. 18; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 84; Schoorl, *Zeitsch. anal. Chem.*, **48**, 215, 220, 672.

SEC. 63.

Summary and Remarks on Group IV.

In the course of an analysis the members of Group IV. are usually precipitated as hydrated sulphides by treating their solutions with ammonium sulphide. Accordingly, in the first place, (I.) we give an outline of the methods by which the metals contained in such precipitates may, as a rule, best be detected and separated from one another when they are all present together, by means of the reactions described in the preceding sections, and then (II) describe a few additional methods which offer special advantages in certain cases.

I. A. 1 Since cobaltous sulphide and nickelous sulphide are only very slightly soluble in dilute hydrochloric acid (especially when hydrogen sulphide is present), whilst the sulphides of iron, manganese, and zinc are readily soluble therein, a method based on these facts is the most suitable means of separating nickel and cobalt, or at least the greater part of them For this purpose, the moist precipitate of the sulphides is treated with a sufficient quantity of a mixture of 5 parts of hydrogen sulphide water and 1 part of ordinary hydrochloric acid of sp. gr. 1 12,[1] with constant stirring but without applying heat

The sulphides of nickel and cobalt remain almost quantitatively in the residue, whilst the other sulphides dissolve as chlorides, with the evolution of hydrogen sulphide The precipitate is separated and washed with water, to which it is advisable to add a little hydrogen sulphide water.

We deal next with the insoluble precipitate, and then with the liquid filtered from it.

2. For the *separation of cobalt from nickel* it is best to dry the filter paper containing the precipitate, to ignite it in the presence of air in a porcelain crucible until the carbon from the paper has been burned, and to heat the residue with hydrochloric acid with the addition of a few drops of nitric acid. If much ferrous sulphide was present, the resulting solution will, as a rule, still contain a small quantity of ferric ion, in addition to the ions of cobalt and nickel Hence, after dilution with a little water, it is treated with a moderate excess of ammonia, filtered if necessary, and the ammoniacal solution evaporated to dryness in a small porcelain dish. The residue is completely freed from ammonium salts by gentle ignition, and dissolved in hydrochloric acid containing a few drops of nitric acid, the nickel and cobalt ions precipitated with sodium carbonate,[2] the

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[1] If the precipitate contains any considerable quantity of the other sulphides, the hydrochloric acid may be diluted with water instead of hydrogen sulphide water, since under those conditions sufficient hydrogen sulphide will be liberated by the acid.

[2] Should no precipitate be produced, the ammonium salts cannot have been completely expelled.

liquid filtered, the precipitate dissolved in the smallest possible quantity of acetic acid diluted with a *little* water, and the solution treated with a concentrated solution of potassium nitrite and a *little* more acetic acid, so that the reaction is strongly acid. Care must be taken throughout the whole process that the volume of liquid does not become too great (Sec. 60, 15) On allowing the liquid to stand in a warm place the cobalt ion separates (soon if a considerable quantity, and after some time if only a small amount is present) in the form of yellow potassium cobaltinitrite. The liquid is filtered after about 12 hours, and nickel ion precipitated from the filtrate by means of potassium or sodium hydroxide. In each case the precipitate should be fused in a borax bead as a confirmatory test (Sec 60, 21, and Sec 59, 25).

Another method is to dissolve the precipitate obtained by means of sodium carbonate in hydrochloric acid, and to test part of the solution for cobalt ion with α-nitroso-β-naphthol (Sec. 60, 18), and another part for nickel ion with dimethylglyoxime (Sec. 59, 19) or dicyanodiamidine sulphate. The use of these reactions may be especially recommended when very small amounts of the cation are to be detected.

3. *Separation of iron.*—The filtrate from the cobalt and nickel sulphide precipitate will contain the iron as ferrous ion, together with the manganous and zinc ions, and any residual traces of cobaltous and nickelous ions. Since iron ion can only be separated readily from the other cations when it is present in the trivalent condition, the liquid is first boiled for a sufficient time to expel the hydrogen sulphide, and nitric acid added to the gently boiling solution until the ferrous ion has been completely converted into ferric ion. (In doubtful cases certainty is attained by testing the liquid with a few drops of potassium ferricyanide solution) The liquid is cooled, and the ferric ion precipitated as basic ferric salt. For this purpose one of the following methods may be chosen :—

(*a*) The free acid is nearly neutralised by the cautious addition of sodium carbonate, but the solution must still remain clear (any precipitate produced being re-dissolved by the addition of a drop of hydrochloric acid), and the liquid is treated with a moderate excess of precipitated barium carbonate, so that some of it remains undissolved, then thoroughly stirred, allowed to settle, and filtered.

(*b*) The solution is diluted to a sufficient extent, and treated with a fairly large quantity of ammonium chloride, and then cautiously with ammonium carbonate (in dilute solution) until the liquid, which must still show an acid reaction, shows signs of becoming turbid, after which it is boiled for a short time, allowed to stand, and filtered while hot.

(*c*) The solution is diluted, sodium carbonate added until the acid is nearly neutralised, and the clear, still perceptibly acid liquid treated with sodium carbonate, heated to boiling point, allowed to stand for a short time, and filtered.

If one of these methods has been used the presence of ferric ion may, as a rule, be recognised at once by the ochre colour of the precipitate. In doubtful cases a little of the precipitate may be dissolved in hydrochloric acid, and the dilute solution tested with potassium ferrocyanide or potassium thiocyanate.

4. *Separation of manganese and zinc.*—The filtrate from the basic ferric salt may now contain manganous ion, zinc ion, and traces of cobaltous and nickelous ions. A good method of separating manganous ion from the other cations may be based upon the solubility of manganous sulphide in acetic acid. The separation by this means is best effected by one of the following methods (preferably after the separation of barium ion by means of sulphuric acid, when barium carbonate has been used for the precipitation of ferric ion (3 (*a*))

(*a*) The solution is treated in a small boiling flask with ammonium chloride, then with ammonia, until the reaction is alkaline, and lastly with ammonium sulphide, allowed to stand in a warm place, and filtered. The precipitate is washed with water to which a little hydrogen sulphide water has been added, the filter containing it spread out in a small basin and treated with a mixture of about equal parts of acetic acid (sp. gr. 1·04) and water, and after about five minutes the liquid is diluted with water and filtered, and the precipitate washed.

(*b*) The following method is more accurate, but somewhat more tedious. The solution is treated with excess of ammonia and then with acetic acid until the reaction is acid, sodium acetate added, a current of hydrogen sulphide introduced into the heated liquid, which is then allowed to stand, and the precipitate filtered off and washed.

In either case the solution, in which there is free acetic acid and hydrogen sulphide, will now contain the manganous ion, and this may be separated as follows:—

(*α*) The solution is treated with ammonia and ammonium sulphide, and the manganous ion thus precipitated as sulphide; (*β*) The solution is concentrated by evaporation, so as to remove the hydrogen sulphide, and the manganous ion precipitated by means of potassium hydroxide as manganous hydroxide (which turns brown on exposure to the air, owing to oxidation); (γ) The solution is treated with a little hydrobromic acid until it is distinctly yellow, and then with ammonia, and the manganous ion precipitated as hydrated dioxide by boiling the liquid. Of these methods the last has the advantage of great sensitiveness, and that, owing to the brownish-black colour of the precipitate, any further test is, as a rule, unnecessary. As a confirmatory test, portions of the compounds precipitated, as described in α, β, or γ, may be fused with sodium carbonate according to Sec. 58, 19.

5 *Detection of zinc.*—The insoluble residue left after the treatment with acetic acid, as in 4 (*a*), or the precipitate produced by means of hydrogen sulphide from the solution acidified with acetic acid, as in 4 (*b*), contains zinc sulphide, the white colour of which is more or less masked by the small amounts of the sulphides of cobalt and nickel which it contains. For the detection of zinc the precipitate is spread out in a porcelain dish and treated with a mixture of about 5 parts of hydrogen sulphide water and 1 part of ordinary hydrochloric acid of sp. gr. 1·12, and after about five minutes the acid solution, which will now contain the zinc ion, is filtered from the undissolved nickel and cobalt sulphides. When the filtrate is treated with sodium acetate the zinc ion is precipitated as white zinc sulphide, free from the traces of nickel and cobalt ions which have been dissolved by the hydrochloric acid, since the sulphides of those metals are not precipitated in the cold under these conditions (Sec. 59, 1, and Sec. 60, 1). If so little cobalt and nickel ions were present that they were not detected in 2, the residue of sulphides obtained in 5 must still be tested for those cations by the methods described in 2.

B. *Method of Bottcher and of Ebler.* (1) In this method a concentrated solution of the chlorides of all the metals of the fourth group is used. Such solution may be obtained by dissolving the sulphide precipitate in concentrated hydrochloric acid, with, if necessary, the addition of a little nitric acid (which, however, must only be employed when complete solution is not effected by hydrochloric acid alone, and then only after complete removal of the hydrogen sulphide), evaporating the solution to dryness, and dissolving the residue in a little water. This solution is treated with 10 c.c. of 3 per cent. hydrogen peroxide solution, and added slowly drop by drop, with continuous stirring, to about 50 c.c. of equal parts of a freshly-prepared 25 per cent. sodium hydroxide solution and 3 per cent. hydrogen peroxide solution, and the whole diluted with water and filtered.

2. The filtrate will contain the zinc ion, and this may be precipitated as white zinc sulphide by means of hydrogen sulphide or ammonium sulphide.

3. The precipitate will contain ferric hydroxide, hydrated manganese dioxide, and cobaltic or nickelic (or nickelous) hydroxide[1] It is dissolved in hot concentrated hydrochloric acid, and the acid solution treated with hydrogen peroxide and poured into a mixture of equal parts of strong ammonia solution and 3 per cent. hydrogen peroxide.

4. The precipitate containing the iron and manganese is dissolved in hydrochloric acid, and the solution freed from chlorine treated in the cold with ammonium chloride and hydroxylamine chloride, and then with excess of ammonia, and heated in a covered vessel on the water-bath. The ferric ion is precipitated as ferric hydroxide, whilst the manganous ion in the filtrate is precipitated as sulphide by means of ammonium sulphide.

5. The filtrate, containing the nickel and cobalt in the form of ammonia complexes, may be treated by one of the following methods: (*a*) It is evaporated to dryness and the residue ignited to remove ammonium salts, or evaporated with fuming nitric acid, and then treated as described above in A. 2 (*b*) The nickel may be precipitated directly by means of dicyanodiamidine sulphate and sodium hydroxide from the filtrate containing the nickel and cobalt ions (because the cobalt ion is present in the trivalent condition and is, therefore, not precipitated by sodium hydroxide from its ammoniacal solution) The cobalt ion may then be precipitated from the filtrate as sulphide by means of ammonium sulphide It may also be precipitated with α-nitroso-β naphthol from another portion of the filtrate still containing nickel ion.

C. 1. The hydrochloric acid solution of the cations may also be treated with ammonia and bromine water, whereby ferric and manganous ions are precipitated, and may then be separated as described above.

2. The solution is treated in the cold with sodium hydroxide, which precipitates the nickel ion as hydroxide. On boiling the filtrate cobalt ion is precipitated as hydroxide. The filtrate from this will still contain zinc ion, and this may be precipitated by means of hydrogen sulphide, after acidifying the solution with acetic acid.

[1] Sec. 59, 9

II. We now describe some other methods which may be used with advantage in certain special cases: (1) If it is a question of separating *small amounts of iron ions* from the other cations of the fourth group, the best method is to treat the solution (which must contain the iron in trivalent form, and must therefore have been oxidised if necessary) in the cold with ammonium chloride and a moderate excess of ammonia, and to filter off rapidly the small amount of precipitated ferric hydroxide. If filtration is delayed, part of the manganous ion will separate as manganous manganic hydroxide with the ferric hydroxide, owing to the action of the atmospheric oxygen. By re-dissolving the precipitate in hydrochloric acid, boiling the solution for a short time, and again precipitating ferric hydroxide in the cold by means of ammonia in excess, the separation of ferric ion from the other cations is rendered almost complete. By adding hydroxylamine chloride or a hydrazine salt the precipitation of manganese may be prevented, and in that case the double precipitation need not be made In the presence of considerable quantities of iron ion, the method cannot be recommended, because in that case a certain amount of the other hydroxides is always precipitated with the ferric hydroxide, with the result that when this method is used small amounts of the other cations may be entirely overlooked

2 If *zinc ion* is to be separated from the other cations of the fourth group, one of the following methods may be used:–

(*a*) The solution is sufficiently diluted, the greater part of any free acid present neutralised with ammonia, ammonium monochloroacetate and some free monochloroacetic acid added, the liquid heated to 50°–60°, and the zinc ion precipitated by means of hydrogen sulphide The other cations remain in solution.

(*b*) The solution is treated with sodium carbonate until a permanent precipitate is just formed, this precipitate dissolved by adding a few drops of dilute hydrochloric acid, sodium thiosulphate added in not too small a quantity, the liquid greatly diluted, and hydrogen sulphide introduced in the cold. The zinc ion is precipitated as zinc sulphide, whilst the other cations remain in solution (J Riban).

(*c*) If a considerable amount of zinc is to be separated from small quantities of the other ions, the solution may also be treated with potassium or sodium hydroxide. On adding this in excess, the precipitated zinc hydroxide is re-dissolved, whilst the hydroxides of the other metals remain as an insoluble residue The zinc ion may be precipitated from this solution by means of ammonium sulphide (*cf.* Part II., Chap. III., Footnote to Rubric No. 50). This method, however, seldom offers special advantages, because some zinc remains in the insoluble precipitate. The method would be quite unworkable if chromic ion were also present, since zinc and chromic ions reciprocally precipitate each other from potassium or sodium hydroxide solutions. The latter difficulty, as also any retention of the zinc by manganese, may be obviated by adding hydrogen peroxide, sodium percarbonate, or bromine to the sodium hydroxide solution, whereby the chromic ion is converted into chromate ion and manganous ion into the tetravalent condition.

3. If a brown coloration is obtained in the filtrate from the precipitated sulphides, the presence of nickel is indicated. In this case, the somewhat tedious method of separating cobalt ion from nickel ion, as given above in A. 2, may sometimes be omitted, since it is often possible when testing a part of the residue obtained in A. 2, after removal of the ammonium salts, to detect the cobalt with certainty in the presence of nickel in a borax bead exposed to the reducing flame. If small amounts of nickel ion are to be detected in the presence of considerable quantities of cobalt ion, it is advisable to use a potassium cyanide solution of the cyanides, which has been treated with sodium hydroxide. The cobalt ion may be detected in a portion of this liquid by means of the red coloration produced by yellow ammonium sulphide, and the nickel ion by the black precipitate of nickelic hydroxide produced by means of chlorine or bromine (Sec 59, 12, and Sec. 60, 12). The different behaviour of the hydroxides of the trivalent metals towards potassium cyanide solution or ammonium chloride and ammonia solution is more suitable for the differentiation than for the separation of nickel and cobalt ions.[1]

Small amounts of nickel ion may also be detected in the presence of cobalt ion by treating the solution with sodium peroxide, thoroughly washing the precipitate of cobaltous and nickelous hydroxides[2] with cold water, and treating it on the filter with a cold saturated solution of oxalic acid, when nickelous hydroxide dissolves. On adding to the filtrate a little potassium ferricyanide and sodium hydroxide, black nickelic hydroxide is precipitated (Benedict, *Chem. Zentralbl.*, 1904, II., 561). For the detection of small amounts of nickel ion in the presence of cobalt ion, the reactions given in Sec. 59, 5 (footnote), 16, and *especially* 18 and 19 are also suitable. For the detection of *small amounts of cobalt ion* in the presence of nickel ion, the reactions Sec. 60, 16, and 18 are applicable.

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[1] With regard to the detection of nickel ion in the presence of cobalt ion, see also Herrenschmidt and Capelle, *Zeitsch anal Chem.*, **32**, 607.

[2] Kassner, *Ibid.*, **34**, 596.

4. For the separation of the members of the fourth group in the presence of *organic non-volatile* substances, methods based upon the preliminary separation of all the cations as sulphides must be used, because the organic substances mentioned would influence or prevent the precipitation of the ions of iron as hydroxide or basic chloride. In the presence of citric acid, however, even these methods are not sufficient, because alkali citrates prevent the complete precipitation of manganous ion as manganese sulphide. Hence, in the presence of citric acid, it is necessary to evaporate the solution with sodium carbonate and to ignite the residue with potassium nitrate, so as to destroy organic substances.

5. *Ferrous and ferric compounds* are detected in the presence of each other by testing for the former with potassium ferricyanide, and for the latter with potassium ferrocyanide or with potassium thiocyanate.

Silicates may be prepared for this test by heating the powder with fused borax in a sealed glass tube. After the decomposition is complete, the tube is sprinkled with water to crack the glass, and is broken after cooling. The substance is treated with hydrochloric acid in a test-tube, and portions of this solution are tested for divalent and trivalent iron as described.

SPECIAL REACTIONS OF THE RARER MEMBERS OF THE FOURTH GROUP.

SEC. 64.

1. Uranium, U, 238.2

Uranium is a greyish-white metal, which has a specific gravity of 18.68, and is very difficult to fuse. It is usually present in its compounds in the tetravalent and hexavalent condition. It is only of rare occurrence in pitchblende, carnotite, and samarskite. Minerals containing uranium and uranium compounds are radioactive. *Uranous oxide*, UO_2, is brown or black, and is dissolved by nitric acid, forming uranous nitrate. *Uranic oxide*, UO_3, is brick-red. *Uranyl hydroxide*, $UO_2(OH)_2$, is yellow. When ignited in the air both the oxide of tetravalent uranium and that of hexavalent uranium yield a blackish-green *uranous uranic oxide*, U_3O_8 (corresponding to pitchblende).

I. **Salts of tetravalent uranium.**—*Uranous salts* are green, and in solution are readily converted into uranyl salts. According to Clemens Zimmermann,[1] pure uranous salts free from hexavalent uranium show the following reactions:

1. *Ammonium sulphide* gives a pale green precipitate, which very rapidly becomes dark and black when boiled.

2. *Potassium and sodium hydroxides* and *ammonia* produce voluminous pale green precipitates of uranous hydroxide, which are insoluble in excess of the precipitant. They rapidly change in the air, being converted first into brownish-black uranic oxide, and, after some time, into yellow alkali uranate.

Notes to 1 and 2. Tartaric acid prevents the formation of precipitates by means of ammonium sulphide, potassium and sodium hydroxides, and ammonia. The liquid does *not darken* in colour.

3. *The carbonates and hydrogen carbonates of potassium and sodium* produce a whitish-green precipitate, which darkens when heated owing to oxidation. The precipitate is soluble in excess of alkali hydrogen carbonate solution, but is partially oxidised and re-precipitated when the liquid is heated.

4. *Ammonium carbonate* produces a similar precipitate soluble in excess of the precipitant. It is not re-precipitated, even on heating the solution.

5. *Barium carbonate* completely precipitates uranous compounds, even in the cold.

6. *Potassium ferrocyanide* produces immediately a yellowish green precipitate, which gradually changes to reddish brown in consequence of oxidation.

7. *Potassium ferricyanide* produces immediately a reddish-brown precipitate.

8. *Hydrofluoric acid* precipitates insoluble uranous fluoride from solutions of uranous salts (Hillebrand; Giolitti, *Zeitsch. anal. Chem.*, **44**, 431)

II. **Salts of hexavalent uranium.**—Hexavalent uranium forms, on the one hand, salts containing the divalent cation $UO^{\cdot\cdot}$ (*uranyl salts*), and on the other hand, salts containing the anion UO''_4, or $U_2O''_7$ (*uranates*). Both forms of the compounds of hexavalent uranium are yellow. Most *uranyl salts* are soluble in water, whilst those which are insoluble therein dissolve almost without exception in hydrochloric acid. The solutions are yellow.

1. When a *sulphuric acid solution* of uranyl salts is heated with *zinc* the yellow colour of the liquid is changed to the green colour of uranous salts.

2. *Hydrogen sulphide* has *no* action upon solutions of uranyl salts.

3. *Ammonium sulphide* produces, after neutralisation of free acid, a precipitate which subsides slowly, and is readily soluble in acids, including acetic acid; its formation is promoted by ammonium chloride and prevented by hydroxylamine hydrochloride. When precipitated in the cold,

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[1] *Zeitsch. anal. Chem.*, **23**, 66. (With regard to the absorption spectrum of uranous salts, see *Ibid.*, p. 220.)

it is of a chocolate brown colour, and contains *uranyl sulphide*, ammonium sulphide, and water. It is insoluble in ammonia solution, but dissolves in colourless or yellow ammonium sulphide containing a little ammonium carbonate, forming a brown solution (Cl. Zimmermann); on washing the precipitate it is gradually converted into yellow uranyl hydroxide. When a solution of a uranium salt which has been treated with ammonium sulphide is boiled, the uranyl sulphide first precipitated is decomposed into sulphur and black uranous oxide, which latter is insoluble in excess of ammonium sulphide (Remelé). The *uranyl sulphide* (but not the precipitate which has been converted into uranous oxide and sulphur) is readily soluble in ammonium carbonate solution. (Essential distinction and method of separating the ions of uranium from those of zinc, manganese, iron, etc.) If the uranyl sulphide remains for a long time in contact with excess of ammonium sulphide, it is converted, in the presence of air, owing to the formation of ammonium thiosulphate, into a red compound, and in the absence of air into a black product of reaction.

4. *Ammonia* and *potassium and sodium hydroxides* produce yellow precipitates of alkali uranates, *e.g.*, $K_2U_2O_7$, insoluble in excess of the precipitant. *Tartaric acid* prevents or influences the precipitation by ammonia, *hydroxylamine hydrochloride* prevents it, whilst *ammonium chloride* promotes it.

5. *Freshly precipitated mercury oxide* precipitates uranium quantitatively from boiling solutions which have been treated with ammonium chloride. (Method of separating uranic ion from strontium, calcium, and alkali ions, and less completely from barium ion. Alibegoff.)

6. *Ammonium carbonate*, and also *potassium or sodium hydroxide carbonates*, produce in solutions of uranyl salts yellow precipitates of *alkali uranyl carbonate*, *e.g.* $2K_2CO_3,(UO_2)CO_3$, *which dissolve readily in excess of the precipitant.*[1] Potassium or sodium hydroxide precipitates the whole of the uranic ion from such solutions.

7. *Barium carbonate* precipitates uranic ion completely, even in the cold. (Essential distinction and means of separation from nickel, cobalt, manganese, and zinc ions.)

8. *Disodium hydrogen phosphate* produces in solutions of uranyl salts containing acetic acid or alkali acetates a yellowish-white precipitate of *uranyl hydrogen phosphate* $(UO_2)HPO_4 + xH_2O$, which is soluble in mineral acids. In the presence of much ammonium salt a precipitate of *ammonium uranyl phosphate*, $(UO_2)(NH_4)PO_4 + xH_2O$, which is of similar colour, is obtained. Heat promotes the separation of both precipitates.

9. *Hydrogen peroxide* produces a yellowish-white precipitate of hydrated *uranium tetroxide*, UO_4, soluble in hydrochloric acid (Fairley, *Zeitsch.*

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[1] The decomposition product uranium X, derived from uranium, is here left as a slight insoluble residue. (Organic solvents, such as acetone, etc., when applied to uranyl nitrate, may also effect a separation from uranium X, which remains undissolved.) Moore and Schlundt, *Phil. Mag.*, (6) **12**, 393; *Chem. Zentralbl.*, 1906, II., 1176. For details of the chemistry of the radio-elements reference may be made to, *e.g.* F. Henrich's book, *Chemie und chemische Technologie radioaktiver Stoffe*, Berlin, 1918.

anal. Chem., **44**, 433). The presence of sulphuric acid or sulphates or of fluorides prevents the precipitation, presumably owing to the formation of complex compounds (Mazzucchelli, *Atti Accad. Lincei Roma* (5), **15**, II., 494; *Chem. Zentralbl.*, 1907, I., 304). *Ammonium carbonate* dissolves this precipitate, forming an intense yellow solution. This reaction is very sensitive. When a solution in sulphuric acid of the precipitate produced by hydrogen peroxide is shaken with *ether* it imparts a *blue coloration* to the latter. *Sodium peroxide* produces in solutions of uranyl salts a yellow precipitate soluble in excess of the precipitant; alcohol precipitates from this solution yellow *sodium peruranate*, $Na_4U_2O_8 + 8H_2O$, which after some time becomes crystalline. If the liquid is boiled before the addition of alcohol, red *uranyl sodium peruranate*, $(UO_2)Na_2U_2O_8$, is precipitated (Kassner, *Zeitsch. anal. Chem.*, **34**, 595). Analogous results are obtained by treating a solution of a uranyl salt with hydrogen peroxide and *potassium carbonate* in solid form or in concentrated solution (J. Aloy, *Zeitsch. anal. Chem.*, **44**, 433).

10. *Ethylenediamine* produces in solutions of uranyl salts, even when extremely dilute, a crystalline yellow precipitate, which is soluble in excess of the resulting uranium compound (J. A. Siemssen, *Chem. Zeit.*, **35**, 139 and 742; *Zeitsch. anal. Chem.*, **52**, 773).

11. *Potassium ferrocyanide* produces a precipitate or at least a reddish-brown coloration. This is a very sensitive reaction. The precipitate dissolves in ammonium carbonate solution, forming a yellow liquid, and is also soluble in hot dilute hydrochloric acid.

12. Solutions of uranyl salts, and in particular of the nitrate, *colour turmeric paper brown*, even in the presence of a little free hydrochloric acid, although the reaction is then less sensitive. Large amounts of mineral acids inhibit the reaction (Cf. Zimmermann). On touching the turmeric paper, which has been turned brown by a uranyl salt solution, with sodium carbonate solution dark brown spots are produced.

13. *Alkanet tincture* becomes green when treated with neutral uranyl nitrate or chloride solution. It shows two characteristic absorption bands at 687 and 631 $\mu\mu$.

14. *Alkali phosphate* and *borax* dissolve uranyl salts in the outer flame, producing yellow beads, which on cooling appear yellowish-green with green fluorescence, whilst in the inner flame they produce green beads.

15. With regard to the *microchemical detection* of uranium ion, see Haushofer, *Mikroskopische Reaktionen*, p. 132, and Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 150.

SEC. 65.

2. Thallium, Tl, 204.

Thallium occurs in crookesite (a copper selenide) and also, though invariably in small quantities, in many varieties of pyrites containing copper, and in many kinds of iron pyrites, in varieties of crude sulphur, and in the deposits of flue dust of the lead chambers, the furnace of which has been charged with pyrites containing thallium ; it is sometimes present in commercial sulphuric and hydrochloric acids, and it has been found in lepidolite, bismuth, and cadmium preparations, in plant ash, and in some mineral waters.

1. Thallium is a soft metal *resembling lead*, having a specific gravity of 11·8 to 11·9, and melting at 301·5° (Roos, *Chem. Zentralbl.*, 1916, I., 1117) ; it volatilises at a red heat, when bent it crackles like tin, becomes coated with oxide when exposed to the air, does not decompose water, and is soluble in dilute acids with the evolution of hydrogen. Thallium is readily soluble in dilute sulphuric and nitric acids, but dissolves with difficulty in hydrochloric acid. It is monovalent or trivalent in its compounds. In its monovalent compounds it has many close analogies with the ions of potassium, whilst in the trivalent compounds it behaves like a heavy metal ion ; the $Tl^{\cdot\cdot\cdot}$ ion forms very stable complex ions.

2. *Thallous oxide*, Tl_2O, is black, fusible, and when fused attacks glass or porcelain. It is soluble in water, yielding a colourless, alkaline, corrosive solution, which absorbs carbon dioxide. It is also soluble in alcohol.

Thallic oxide, Tl_2O_3, is blackish-violet and insoluble in water ; *thallic hydroxide* is brown. Thallic oxide is hardly attacked by concentrated sulphuric acid in the cold, but combines with it on heating. If the heating is continued for a long time, thallous sulphate is formed, and oxygen liberated. Thallic oxide reacts with hydrochloric acid to form the corresponding chloride, which may be separated in the form of colourless, readily soluble crystals. When it is heated, chlorine escapes, while compounds of thallous and thallic chlorides are formed.

3. The *thallous salts* are colourless ; some (the sulphate, nitrate, monohydrogen phosphate, tartrate, and acetate) are readily soluble, others (carbonate, neutral phosphate, chloride) sparingly soluble, and others (iodide) almost insoluble. When solutions of thallous salts are boiled with nitric acid, the thallous ion is not converted into the trivalent condition, which reaction, however, takes place quantitatively when the solution is boiled with *aqua regia*.

The *thallic salts* are hydrolytically dissociated by water, with the separation of thallic hydroxide ; alkali hydroxides precipitate thallic hydroxide from their acid solutions ; hydrogen sulphide converts them into thallous salts, whilst sulphur separates, and with potassium iodide they yield iodine and thallous iodide. They are not precipitated by hydrochloric acid.

4. *Potassium and sodium hydroxides* and *ammonia* do not produce precipitates in aqueous solutions of thallous salts.

5. *Alkali carbonates* precipitate *thallous carbonate*, but only from quite concentrated solutions, since 100 parts of water at 18° dissolve 5·23 parts of thallous carbonate.

6. *Hydrochloric acid* produces in solutions which are not too dilute a white precipitate of thallous chloride, which rapidly subsides, does not

alter on exposure to light, and is only sparingly soluble in water, even less so in dilute hydrochloric acid.

7. If *chlorine gas* is introduced into solutions of thallous salts white thallous chloride is precipitated, and this becomes first brown and then dissolves, owing to the formation of thallic chloride. (Suitable method of separation from silver.)

8. *Potassium iodide* produces in very dilute solutions a light yellow precipitate of *thallous iodide*, which is only slightly soluble in water (1 : 17,000), and still less soluble in excess of potassium iodide solution. The precipitate dissolves with difficulty in sodium thiosulphate solution in the cold. (Distinction from lead iodide. E. A. Werner.) *Owing to its sensitiveness this reaction is the most suitable for the detection of thallium by the wet method*; if ferric ion is present, it must first be reduced by means of sodium sulphide.

9. *Platinohydrochloric acid* gives a sparingly soluble, pale orange, precipitate of *thallous platinochloride*, Tl_2PtCl_6, in solutions of thallous salts which are not too dilute.

10. *Sodium cobaltous nitrite reagent* (*i.e.* sodium nitrite, cobaltous chloride, and acetic acid) produces a sparingly soluble (1 : 10,000) light red precipitate of thallous cobaltic nitrite, $Tl_3Co(NO_2)_6$, in solutions of thallous salts.

11. *Hydrogen sulphide* does not produce a precipitate in solutions strongly acidified with mineral acids, unless arsenic, antimony, or copper ions are present, in which case thallous sulphide is precipitated simultaneously with the other sulphides. *An incomplete precipitate* is produced in *neutral* or *very slightly acid* solutions, but *the whole of the thallium ion* is precipitated as black *thallous sulphide* from an *acetic acid* solution of thallous salts.

12. Colourless *ammonium sulphide*, and also *hydrogen sulphide from alkaline solutions*, precipitates the whole of the dissolved thallium ion as black thallous sulphide, which, especially when heated, readily agglomerates into lumps. This precipitate is insoluble in ammonia, alkali, ammonium sulphide, and potassium cyanide solutions; it is rapidly oxidised to thallous sulphate in the air, is readily soluble in dilute hydrochloric, sulphuric, and nitric acids, but only dissolves with difficulty in acetic acid. When heated, thallous sulphide first melts and then volatilises.

13. *Zinc*, and also *magnesium*, precipitates metallic thallium in the form of black, flake-like crystals from solutions of thallous salts.

14. Thallium compounds impart an intense green colour to colourless *flames*. The spectrum of the thallium flame shows only a single, highly characteristic, fine *emerald green line* (535·06$\mu\mu$, *cf.* the table of spectra). In the case of small amounts of thallium, the flame coloration only lasts for a short time. As a rule, spectrum analysis affords the best means of detecting thallium. Pyrites containing thallium often show the green spectrum line immediately; in the case of crude sulphur, thallium is best detected by extracting most of the sulphur by means of carbon bisulphide, and then testing the residue. When a large amount of a sodium salt is

present, but only a very small amount of a thallium compound, the thallium spectrum can only be rendered visible by introducing a small quantity of the moistened substance into the flame, and then observing the resulting spectrum. If traces of thallous platinochloride are present, together with large amounts of potassium, rubidium, and caesium platinochlorides, in a precipitate produced by means of platinohydrochloric acid, the precipitate is boiled twenty-five to fifty times with successive small quantities of water, and the liquid decanted each time. The final residue from these extractions will then show the thallium line transitorily.

15. For the *microchemical detection* of thallium, see Haushofer, *Mikroskopische Reaktionen*, p. 125, and Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 40.

SEC. 66.

3. Indium, In, 114·8.

Indium was first discovered in Freiberg zinc blende and the zinc prepared from it, and subsequently in some other zinc blendes and in tungsten ore.

1. *Indium* is a white, very lustrous metal resembling platinum in its colour. It is very soft, ductile, makes a mark on paper, and can be polished. It is slowly oxidised on contact with air and water, but less readily than zinc. Its specific gravity is 7·28. Indium melts at 155°; when heated on charcoal by means of the blowpipe, it forms a lustrous metallic film, colours the flame blue, and yields a deposit which is dark yellow while hot and pale yellow on cooling, and can be volatilised with difficulty by means of the blowpipe flame. Indium dissolves slowly in the cold, more rapidly on heating, in dilute hydrochloric and sulphuric acids, with the evolution of hydrogen; when treated with cold concentrated sulphuric acid it also liberates hydrogen, while anhydrous indium sulphate separates; indium is also readily soluble in nitric acid, even when cold and dilute. Indium, as is shown by its chlorides, is *monovalent*, *divalent*, and, in most of its compounds, *trivalent*. Only the trivalent compounds are stable in aqueous solution.

2. *Indium oxide*, In_2O_3, is reddish-brown while hot, but light yellow when cold, and it does not colour glass fluxes. When ignited with hydrogen or with charcoal it is readily reduced, and if a flux is also present, metallic globules are obtained. The ignited oxide dissolves slowly in cold, but rapidly and completely in hot, acids.

3. *Indium salts* are colourless; the sulphate and nitrate, and also the volatile hydroscopic chloride, are readily soluble in water.

4. *Potassium and sodium hydroxides* and *ammonia* precipitate from solutions of the salts a voluminous white hydroxide resembling aluminium hydroxide in appearance. Tartaric acid inhibits the precipitation. The precipitate is soluble in solutions of potassium and sodium hydroxides, but the resulting solution soon becomes turbid, and when boiled or treated with ammonium chloride gives a precipitate of indium hydroxide. *Ammonia solution* does not dissolve the hydroxide.

5. *Alkali carbonates* give a gelatinous white precipitate of indium carbonate. When freshly precipitated, this dissolves in ammonium carbonate solution, but not in potassium or sodium carbonate solution; on boiling its ammonium carbonate solution it is re-precipitated.

6. *Barium carbonate* precipitates the whole of the indium in the form of basic salts when boiled with solutions of indium salts, or even when digested with them in the cold. (Fundamental distinction and means of separation from zinc, manganese, cobalt, nickel, and ferrous ions.)

7. *Disodium hydrogen phosphate* gives a voluminous white precipitate

8. *Alkali oxalates* produce a crystalline precipitate in concentrated neutral solutions.

9. *Sodium acetate* precipitates indium sulphate from a nearly neutral boiling solution of indium sulphate.

10. *Hydrogen sulphide* precipitates the whole of the indium as yellow, possibly hydrated *indium sulphide*, In_2S_3, from neutral or acetic acid solutions (even those in which the acetic acid is present in large excess), it produces no precipitate in solutions strongly acidified with mineral acids, if at all concentrated, but on making the solutions very dilute yellow indium sulphide is precipitated.

11. *Hydrogen sulphide* produces in *alkaline solutions* and *ammonium sulphide* in neutral solutions a white precipitate (possibly *indium hydrosulphide* or *ammonium indium sulphide*). When yellow indium sulphide is boiled with yellow ammonium sulphide, it, too, becomes white and partially dissolves On cooling the liquid, a voluminous white precipitate is formed, which is similar to that obtained by direct precipitation with ammonium sulphide.

12. *Potassium ferrocyanide* gives a white precipitate.

13. *Potassium ferricyanide*, *thiocyanate*, and *dichromate* do not give precipitates, but *potassium chromate* produces a yellow precipitate.

14 *Zinc* precipitates metallic indium in the form of white lustrous flakes.

15. On introducing an indium compound into a colourless flame it colours the flame a characteristic bluish-violet. Two distinctive blue lines may be observed in the *spectrum* (α 451·1 $\mu\mu$, and β 410·1 $\mu\mu$. See Spectrum table). If the chloride is used, these appear with greater brilliancy, especially the α-line, but are very fugitive. Indium sulphide is most suited for a longer examination of the indium spectrum.

16. For the *microchemical detection* of indium, see Huysse, *Zeitsch. anal Chem.*, 39, 10, and Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 82.

SEC. 67.

4. Gallium, Ga, 69·6.

1. *Gallium* is widely distributed, but only in small quantities. It has been found in many zinc blendes and bauxites, and also in some other minerals. Gallium is a white metal; it is silver-white in the fused condition, but on solidification becomes crystalline, bluish-white, and less

lustrous. It melts at 30·15°, and has a specific gravity of 5·956 at 24·5°. It is hard, not very ductile, does not alter at the ordinary temperature, is only slightly oxidised when heated to redness, and does not volatilise at that temperature. Water, even when boiling, is not decomposed by gallium. Nitric acid has no appreciable action upon the metal in the cold, but when heated dissolves it, with the evolution of red vapours. It is readily soluble in hydrochloric acid and in potassium hydroxide and ammonia solutions, with the evolution of oxygen. Gallium is *divalent* and *trivalent* in its compounds.

2. The *gallous compounds* are unstable and have reducing properties. *Gallic oxide*, Ga_2O_3, is white, as is also its *hydroxide*. On heating the oxide to redness in a current of hydrogen, it sublimes, with partial reduction, probably to a lower oxide.

3 The *gallic salts* are colourless or white; the sulphate and nitrate dissolve readily in water, and decompose on ignition; the sulphate combines with ammonium sulphate to form an alum. On boiling the solutions of the sulphate or of the alum, hydrolysis takes place and causes basic salts to separate. Gallium combines with chlorine to form gallous chloride, $GaCl_2$ (which is easily oxidisable) and gallic chloride, $GaCl_3$. The latter is a colourless, deliquescent mass, which melts at 75° and boils at 215°–220°. The volatility of gallic chloride is manifested even on evaporating solutions containing hydrochloric acid. If, however, sulphuric acid is added to the solutions, no loss of gallium takes place, either during the evaporation of the liquid, or on igniting the residue at a dull red heat (Lecoq de Boisbaudran).

4 *Alkali hydroxides* and *ammonia* produce a white flocculent precipitate of gallic hydroxide, readily soluble in excess of the precipitant, in aqueous solutions of gallic salts. But if a solution is treated with excess of ammonia and boiled for a short time, the whole of the gallic ion is precipitated as hydroxide. Tartaric acid prevents the precipitation with ammonia

5 *Alkali carbonates* produce white precipitates: that produced by ammonium carbonate is soluble in excess of the precipitant.

6 *Barium carbonate* completely precipitates gallic ion, even in the cold.

7. *Hydrogen sulphide* does not produce a precipitate in acid solutions of gallic salts, nor is a precipitate formed in acetic or tartaric acid solution, even in the presence of ammonium acetate or tartrate, provided that no other cations capable of being precipitated are present[1] In the presence of zinc, silver, copper, manganese, iron, or arsenic ions, hydrogen sulphide precipitates the whole of the gallic ion, together with the sulphides of the other metals, from solutions acidified with weak acids (whether as sulphide or hydroxide is not certain). The gallium precipitate is white.

8. *Ammonium sulphide* also precipitates gallic ion only in the presence of the metal ions mentioned.

9. *Ammonium acetate* precipitates nearly the whole of the gallic ion,

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[1] The older observations of Lecoq de Boisbaudran, that under certain conditions the sulphide was precipitated, appear to be erroneous It was probably a question of the hydrolytic separation of the hydroxide.

owing to hydrolytic dissociation, from a dilute boiling solution, but only when the precipitate is present in not too great a quantity.

10. *Cupric hydroxide*, and also *manganous sulphide*, completely precipitate gallic ion as hydroxide, in consequence of hydrolytic dissociation. When manganous sulphide is used, hydrogen sulphide is liberated. Gallic ion may be separated from many cations, *e g.* lead, cobalt, nickel, iron, thallium, and beryllium ions and the ions of the rare earth metals, by means of cupric hydroxide.

11. *Potassium ferrocyanide* produces a bluish precipitate (the colour being probably due to the presence of iron compounds), which is less soluble in hydrochloric acid than in water, and only dissolves when boiled with a large excess of the former. This is a very sensitive reaction.

12. Gallium compounds show a *spectrum* characterised by two violet lines (between G and H, 417·0 and 403·1$\mu\mu$), but this is only very distinct in the spark spectrum; if a gallium compound is introduced into a *Bunsen* flame, only one of these lines can be faintly discerned.

SEC 68.

5. Vanadium, V, 51.

Vanadium is a silvery-white to light grey metal, which occurs as vanadate in certain rare minerals in considerable proportion, and in small amounts is also present in many rocks, clays, and in plant ash. It is also found in many metallurgical products, and sometimes in caustic soda, etc. It is present in its compounds in the *divalent*, *trivalent*, *tetravalent*, and *pentavalent* condition. Its specific gravity is about 5·8, and its melting point 1715° (Ruff and Martin). The oxides corresponding to the different conditions of valency are *vanadous oxide*, VO, *vanadic oxide* (vanadium trioxide), V_2O_3, *vanadium tetroxide*, V_2O_4, also termed *vanadyl oxide*, and the *pentoxide* V_2O_5 (vanadic anhydride).

Vanadous oxide is dark grey, with a metallic lustre, and is insoluble in water, but dissolves in dilute acids to form blue solutions of the corresponding vanadous salts (with a small amount of vanadic salts), which bleach organic colouring matters by reduction.

Vanadic oxide is black, insoluble in acids (with the exception of hydrofluoric acid and nitric acid), and in alkali hydroxide solutions, not reduced by ignition in hydrogen, and slowly changes in the air to vanadyl oxide Acid solutions of vanadic salts are green.

Vanadyl oxide is dark blue, whilst acid solutions containing tetravalent vanadium ion are bright blue.

When heated with nitric acid or *aqua regia*, or fused with potassium nitrate, or ignited in oxygen or air, the lower oxides are converted into the *pentoxide*. This is a non-volatile, fusible substance, which solidifies in crystalline form, and has a yellow-ochre colour. When ignited at a red heat in hydrogen it is converted into vanadic oxide. When exposed to moist air it absorbs water (forms vanadic acid), and is transformed into a dull red colloidal mass. On contact with a little water it yields a sticky mass, which dissolves in a large quantity of cold water (more readily in hot water), forming a blood-red hydrosol (A Ditte, Biltz[1]). *Vanadic acid* strongly reddens moist litmus paper. Pentavalent vanadium forms, on the one hand, salts in which it is present in the form of the cations $VO^{\cdot\cdot\cdot}$ and $VO^{\cdot}_2$, and, on the other hand, salts which contain the vanadium in the anion (*cf. infra*, under β).

(α) *Solutions of salts with pentavalent vanadium in the cation* —The stronger acids dissolve vanadium pentoxide, forming red or yellow solutions, which contain the cations $VO^{\cdot}_2$, $VO^{\cdot\cdot\cdot}$, and possibly also to a small extent $V^{\cdot\cdot\cdot\cdot\cdot}$; these gradually become green on exposure to air owing to reduction.

1 When a cold acid solution containing vanadic cation is gradually treated with *ammonia*, the liquid invariably becomes distinctly yellow up to the point when the reaction becomes alkaline (Carnot). *Potassium and sodium hydroxides* produce brown precipitates, which dissolve in excess of the precipitant to form yellowish-green solutions

2 When zinc is introduced into a hot dilute sulphuric acid solution, the colour of the liquid is first changed through green into blue (reduction to the tetravalent condition), then through greenish-blue into green (reduction to the trivalent condition), and finally through violet into lavender-blue (reduction to the divalent condition) *Ammonia* precipitates brown, readily oxidisable, vanadous hydroxide from this last solution.

3 *Sulphur dioxide, hydrogen sulphide* (with separation of sulphur), *oxalic acid*, etc , reduce acid solutions containing vanadium cations, but only up to the tetravalent condition, and thence the liquids only become blue On boiling vanadium pentoxide with *concentrated hydrochloric acid*, chlorine is evolved and chlorides or oxychlorides are formed, some of which contain pentavalent and others tetravalent vanadium (Rosenheim).

4 *Ammonium sulphide* produces a brown precipitate of vanadium sulphide (V_2S_5), which dissolves with some difficulty in excess of the precipitant, forming a red brown solution Acids precipitate brown vanadium sulphide from this solution.

5 *Potassium ferrocyanide* produces a flocculent green precipitate which does not dissolve in acids.

6 *Tannic acid* produces a blue-black precipitate in solutions which contain only a little free acid.

7. On treating an acid solution containing vanadium cation with alkali carbonate until the free acid is nearly neutralised, and then with *mercurous nitrate and an excess of precipitated mercuric oxide*, the vanadium ion is completely precipitated as *mercurous vanadate*. On igniting the precipitate vanadium pentoxide is obtained.

(β) *Vanadates* —Pentavalent vanadium forms a whole series of different and especially of complex anions, of which only the ortho-, pyro-, and metavanadates, VO_4''', V_2O_7'''' and VO_3', can be mentioned here. Vanadium minerals usually contain ortho salts. The soluble ortho salts are converted even on standing in aqueous solution, through hydrolysis, and the insoluble salts on the addition of acid, into vanadates containing a smaller cation, and eventually into metavanadates. The same remark applies to the pyrovanadates, in the solutions of which metavanadates are readily formed, even on the introduction of carbon dioxide. Alkali vanadates are obtained by dissolving vanadium pentoxide in potassium or sodium hydroxide solution, or by fusing vanadium pentoxide with alkali carbonates or nitrates. The solutions are colourless.

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[1] *Ber.*, 37, 1098.

1. On introducing solid *ammonium chloride* into a neutral or alkaline solution of a vanadate previously heated to 30°–40°, the whole of the vanadate ion separates as colourless crystalline *ammonium metavanadate*, which is insoluble in ammonium chloride solution, and which, when ignited in oxygen, leaves a residue of pure vanadium pentoxide This is a particularly characteristic reaction

2. Solutions of the alkali metavanadates are reddened by *strong acids*, owing to the formation of divanadates (condensed in the manner of dichromates).

3. *Barium chloride*, but not strontium or calcium chloride (distinction from phosphate and arsenate ions. Carnot), *silver nitrate*, and *lead acetate* produce in solutions of alkali (meta) vanadates yellow precipitates, which become colourless on standing, and more rapidly when heated.

4 The following reactions enable the different vanadates to be distinguished. Copper salts give with metavanadates a pulverulent precipitate varying from blue to yellow, and with orthovanadates an apple-green precipitate. Lead salts give a white precipitate, and silver salts an orange-red precipitate with orthovanadates, the latter being characteristic of these salts (*cf* Chilesotti, Abegg's *Handbuch*, Vol. III, 3, pp. 757, 765).

5. Soluble *uranyl salts* precipitate *uranyl ammonium vanadate*, $(UO_2)NH_4VO_4 + H_2O$, from an ammoniacal solution (or also from one slightly acidified with acetic acid) which has been treated with ammonium acetate. (Method of separating vanadate ion from the ions of the alkalis and earths and from manganese, zinc, and cupric ions.)

6. A boiling solution of *manganous chloride* containing ammonium chloride precipitates *manganous vanadate* from a boiling vanadate solution which has been treated with ammonium chloride and ammonia. (Method of separating vanadate ion from molybdate ion)

7. When mixed with *aniline hydrochloride* alkali vanadate solutions yield vanadium tetrachloride and *aniline black*.

8. Ammonium sulphide acts in the same way as upon the compounds mentioned in (*a*).

9. The same remark applies to *tannic acid* in the presence of acetic acid.

10. On shaking an acidified solution of an alkali vanadate with *hydrogen peroxide* the solution becomes red, or when very dilute, brownish-pink, owing to the formation of *pervanadate* If the liquid is then shaken with ether it retains its colour, while the ether remains colourless. This is a *very sensitive reaction* (Werther). The disturbing influence of iron ion may

be eliminated by the addition of phosphoric acid. Excess of hydrogen peroxide produces partial decolorisation (A. Weller)

11. A solution of vanadium pentoxide in concentrated sulphuric acid gives with *strychnine sulphate* a bluish-violet coloration, subsequently changing to pink. This is a very sensitive reaction.

12 *Borax* dissolves vanadates in the inner and outer flame, forming transparent beads. In the outer flame these are yellow, orange, or dark yellowish-brown while hot, and colourless (or yellow when a large amount of vanadate is present) when cold; in the inner flame they are a fine green, or brownish in presence of a large amount, and then only appear green after cooling The *alkali phosphate* bead is brownish-red in the outer flame when hot (sensitive reaction) and orange to yellow when cold. In the inner flame the bead appears brownish-green while hot, and is the same colour after cooling.

13 For the *microchemical detection* of vanadium, see Haushofer, *Mikroskopische Reaktionen*, p 133, and Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p 139.

FIFTH GROUP.

Ions of the heavy Metals with Sulphides insoluble in Acids and Alkali Sulphide Solutions.

Members of frequent occurrence: **Silver, Mercury** as **mercurous** and **mercuric ions, Lead, Bismuth, Copper, Cadmium.**

Members of rarer occurrence: **Ruthenium, Rhodium, Palladium, Osmium.**

SEC. 69

Characteristics of the Group

Position in the periodic system.—The fifth analytical group includes a whole series of heavy metals, which all occupy positions in the middle of the different great periods. Of the members of the first great period, copper, which is considerably more "noble" (*i e* less strongly electro-positive) than its neighbours in this period, belongs to this group, whilst the remainder belong to the fourth analytical group. Then come the elements which occupy adjoining positions in the middle of the second great period: ruthenium, rhodium, silver, and cadmium; whilst from the middle of the third and fourth great periods come the elements: osmium, mercury, lead, and bismuth, interrupted only on the one hand by the elements: iridium, platinum, and gold, which are again very closely related to each other, and, on the other hand, by thallium. If we take into consideration the fact that the boundaries of Groups IV and V. (or of V. and VI.) are by no means sharp, the similar behaviour of the metals occupying positions in the middle of the great periods and following each other in the order of their atomic weights becomes still more evident. They are more "noble" (less strongly electro-positive) on the one hand, in proportion as they approach more nearly to the *middle* of the great periods, and on the other hand, in proportion to the magnitude of their atomic weights The salts of all the members of the fifth analytical group, with the exception of those of silver, show a tendency, though not a pronounced one towards hydrolysis

Analytical character of the Group. -The sulphides of the metals of the fifth group are insoluble both in dilute acids and in alkali sulphide solutions ;[1] hence the ions of this group are completely precipitated by hydrogen sulphide from their solutions, whether these are neutral or contain free acid (in moderate quantity) or free alkali

The fact that the solutions of ions of the fifth group yield precipitates with hydrogen sulphide, even in the presence of a free strong acid, distinguishes them from the ions of the fourth group, as indeed from those of all previous groups (see p. 217, footnote 2, and the other references given there).

A better survey of the ions of frequent occurrence of this group may be obtained by classifying them into -

1. *Ions precipitated by hydrochloric acid :* Silver, mercurous and lead ions.
2. *Ions not precipitated by hydrochloric acid :* Mercuric, cupric, bismuth, and cadmium ions.

Attention must be directed to lead ion in both divisions, because the sparing solubility of its chloride makes it possible for it to be mistaken for mercurous or silver ions, but does not afford the means of separating it completely from the ions of the second division.

Special Reactions of the Members of the Fifth Group of Frequent Occurrence.

First Division

Ions precipitated by hydrochloric acid.

Sec. 70.

(a) Silver, Ag, 107·88.

1. *Silver* is *monovalent.* Metallic silver is white, very lustrous, moderately hard, very ductile, and fuses with some difficulty at 962°. Its specific gravity is 10·5. It does not become oxidised on exposure

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[1] Compare, however, the behaviour of copper, mercury, and bismuth, to which this rule is only partially applicable

to the air. Silver dissolves readily in dilute nitric acid, and, if finely divided, is somewhat soluble in dilute (1 : 1) sulphuric acid (Carey Lea). It dissolves in hot concentrated sulphuric acid, with the evolution of sulphur dioxide, but is insoluble in hydrochloric acid

2 *Silver oxide*, Ag_2O, is a greyish-brown powder, which is not absolutely insoluble in water, and dissolves readily in dilute nitric acid. It is a strong base When heated it is decomposed, as is also the peroxide, Ag_2O_2, into oxygen and metallic silver. Silver does not form a hydroxide.

3 The *salts of silver* are not volatile, and are usually colourless; many of them become black on exposure to the light The soluble neutral salts do not affect litmus paper, they are decomposed on ignition

Silver salts are decomposed by many reducing agents, with the separation of metallic silver, as *e.g.* silver chloride by sodium hydroxide solution and sugar, or by formaldehyde, ammoniacal or acetic acid solutions of silver salts by hydrazine or hydroxylamine salts (Knoevenagel and Ebler); silver solutions treated with sodium acetate and boiled with hydroquinone (distinction from lead ion) (Ladholm, *Chem Zentr.*, 1905, I, 771); ammoniacal solutions when heated with fairly concentrated potassium hydroxide solution and a few drops of glycerin (E Donath, *Chem Zeit*, 32, 629). (Method of detecting very small quantities of silver ion, *cf* also 11 and 12.)

4 **Hydrogen sulphide** and also **ammonium sulphide** produce in *solutions of silver ion* a *black precipitate* of *silver sulphide*, Ag_2S, which is insoluble in dilute acids, alkali hydroxide, and alkali sulphide solutions, but dissolves in potassium cyanide solution. It is readily decomposed by boiling nitric acid and dissolves, while sulphur separates

Ammonium thioacetate also precipitates silver sulphide.

5 **Sodium thiosulphate,** when added in *small proportion*, produces a *white precipitate, which on heating is converted into black silver sulphide. The white precipitate is soluble in excess of the precipitant*, forming a solution, which, in the absence of free acid, remains clear even when boiled. In the presence of free acid silver sulphide is precipitated from the hot liquid.

6 **Potassium** and **sodium hydroxides** precipitate *silver oxide*, Ag_2O, in the form of a greyish-brown powder, which does not dissolve in excess of the precipitant, but is readily soluble in ammonia solution.

7 **Ammonia** produces a brown precipitate of silver oxide, but

only when it is added in very small proportion to neutral solutions of silver salts. This precipitate is *readily* soluble in excess of ammonia solution, *silver ammonium hydroxide*, $Ag_n(NH_3)_{n+1}(OH)_n$, being formed. *No* precipitate is formed in *acid* solutions of silver salts.

8. **Hydrochloric acid** and **soluble chlorides** produce a *white caseous precipitate of silver chloride*, AgCl. When the solution is very dilute only a bluish white opalescence is at first produced, but on standing for some time in a warm place the silver chloride collects at the bottom of the vessel. Silver chloride, when exposed to the light, changes from white to violet and finally black, meanwhile losing chlorine. *It is insoluble in nitric acid, but dissolves readily in ammonia solution*, probably as silver di-ammonium chloride $Ag(NH_3)_2Cl$. It may be separated again from this compound by means of acid. Concentrated hydrochloric acid and concentrated solutions of alkali chlorides dissolve silver chloride to a very appreciable extent, especially on heating, but on diluting the solution the silver chloride is re-precipitated. *Potassium cyanide* and *sodium thiosulphate* readily dissolve silver chloride. When heated, silver chloride melts without decomposition, and on cooling yields a translucent horn-like mass. Silver chloride is reduced by zinc and dilute sulphuric acid to metallic zinc, while zinc chloride is formed. It is also reduced to silver when ignited in a current of hydrogen or fused with sodium carbonate.

9. *Potassium iodide* produces a white precipitate of *silver iodide*, AgI.

10. *Potassium chromate* produces in solutions, which are not too dilute, a dark brownish-red precipitate of *silver chromate*, Ag_2CrO_4, which is readily soluble in nitric acid, dilute sulphuric acid, and ammonia solution.

11. On treating a neutral or ammoniacal solution of a silver salt with a clear solution of **ferrous sulphate** to which **tartaric acid** and **excess of ammonia** have been added, a *finely pulverulent black precipitate separates, even when the solution was very dilute*. Further investigation is required to determine whether this precipitate is silver suboxide, Ag_4O, or, as appears probable from the work of Friedheim, is a mixture of silver and silver oxide contaminated with organic matter. *Ferrous sulphate by itself* precipitates metallic silver from neutral solutions of silver salts in the form of a grey precipitate. This precipitation takes place gradually in the cold, but more quickly on heating. The separated silver sometimes adheres as a mirror to the sides of the glass vessel.

12. On adding *chromic nitrate* and *alkali hydroxide* to a solution of a silver salt, metallic silver separates as a black precipitate (or in the case of very small quantities of silver as a brownish turbidity). This is a very sensitive reaction, which is suitable for the detection of small amounts of silver in metal objects. A little of the substance is filed off and dissolved in nitric acid (Malatesta and Di Nola, *Chem. Zentr.*, 1913, II., 955).

13. When solid silver compounds are mixed with **sodium carbonate** in a hollow on charcoal and exposed to the **inner blowpipe flame,** *lustrous white malleable metallic globules* are obtained, with or without the simultaneous formation of a *dark red deposit*. The reduction is also easily effected on charcoal sticks (p. 88).

14. Silver compounds dissolve in **alkali phosphate** and **borax** to form beads which are yellowish to opalescent in the outer flame, and greyish-white in the reducing flame.

15. For the *microchemical detection* of silver, see Haushofer, *Mikroskopische Reaktionen*, p. 117; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 120; Streng, *Ber.*, **18**, Ref. 315. Schoorl, *Zeitsch. anal. Chem.*, **47**, 221.

SEC. 71.

(b) Mercury, Hg, 200·6 (as mercurous ion, $Hg_2^{\cdot\cdot}$).

Mercury is *divalent*, and forms two series of compounds: the mercurous compounds with the cation $Hg_2^{\cdot\cdot}$, and the mercuric compounds with the cation Hg. Since these two series of compounds are sharply differentiated analytically, they are dealt with in separate sections. The *mercurous compounds are first described.*

1. *Metallic mercury* has a specific gravity of 13·5, is silvery-white, mirror-like, liquid at the ordinary temperature, solidifies at −39°, and boils at 357·3°. It dissolves in cold dilute nitric acid to form mercurous nitrate, and in the hot concentrated acid to form mercuric nitrate. It is insoluble in hydrochloric acid, and only dissolves with difficulty when potassium chlorate is added to that acid (Lecco). It does not dissolve in dilute sulphuric acid. Concentrated boiling sulphuric acid dissolves it, whilst highly concentrated acid has some solvent action, even in the cold, sulphur dioxide being formed.

Mercury vapour, even when present only in slight traces, may be easily detected by causing it to act upon paper upon which stripes have been made with ammoniacal silver solution. These are soon turned black, owing to the reduction of the silver salt (Merget). Or the vapour may be brought into contact with a solution of auric chloride, free from nitric acid, and is then absorbed, with the formation of mercuric ion and separation of metallic gold, which separates in a film or spots and streaks (Barfoed).

Mercury vapour in the air may be detected by passing the air over genuine gold-leaf, and introducing this into a Geissler tube provided with the necessary stopcocks. The air is first removed from this by repeatedly exhausting it and filling it with hydrogen, and on then exhausting the tube, conducting an induction current through it, and examining it with the spectroscope, the characteristic green line 516$\mu\mu$, and also in the presence of a considerable quantity of mercury the blue line 456$\mu\mu$, may be recognised. This is a very sensitive method (*cf* Treadwell, *Qualitative Analysis*, 6th ed , p. 475).

2. *Mercurous oxide*, Hg_2O, is a black powder, which volatilises with decomposition when heated, and is readily soluble in nitric acid. Mercurous hydroxide is not definitely known to exist, and in any case is unstable

3. The *mercurous salts* volatilise with decomposition on heating. Mercurous chloride (calomel) and mercurous bromide volatilise *without decomposition*. Most of the mercurous salts are colourless The soluble salts in the neutral condition redden litmus, owing to hydrolysis. They are converted by the action of a large amount of water into basic salt with the liberation of acid, *e.g.*, $Hg_2(NO_3)_2 + H_2O = Hg_2(OH)NO_3 + HNO_3$. Hence, when mercurous nitrate is treated with water free from acid, part of it separates as a yellow basic salt, whilst the remainder dissolves owing to the action of the acid produced.

4. **Hydrogen sulphide** and also **ammonium sulphide** produce *black precipitates*, which are *insoluble in dilute acids* and also in *potassium cyanide solution*. These precipitates (when ammonium polysulphide has not been used) consist of *mixtures of mercuric sulphide*, HgS, with *finely divided metallic mercury*. A solution of sodium monosulphide dissolves such precipitates in the presence of a little sodium hydroxide, while metallic mercury is separated and sodium polysulphide solution dissolves them without such separation. The resulting solution contains mercuric sulpho anions; on the addition of ammonium chloride, mercuric sulphide is precipitated. Boiling *dilute* nitric acid dissolves the metallic mercury as mercuric ion from the precipitate produced by hydrogen sulphide, whilst the mercuric sulphide remains undissolved. The mercury reacts with boiling *concentrated* nitric acid to form a white double compound, $2HgS + Hg(NO_3)_2$, and it is readily decomposed

and dissolved by *aqua regia* or by hydrochloric acid and potassium chlorate.

Sodium thiosulphate produces a black precipitate of sulphide in acid solutions of mercurous salts.

5. **Potassium hydroxide** and **sodium hydroxide** give a *black* precipitate of mercurous oxide containing metallic mercury and mercuric oxide; this precipitate is insoluble in excess of the precipitant. **Ammonia** produces in very dilute solutions a *grey* precipitate and in concentrated solutions a *black* precipitate, which are soluble, with decomposition, in excess of the precipitant. When the ammonia was added in excess, these precipitates consist of mixtures of finely divided mercury with the white precipitates which ammonia produces in the solutions of the respective mercuric salts (Lefort, Barfoed) (*Cf.* Sec. 74, 5.

6 **Hydrochloric acid** and **soluble chlorides** produce an *exceedingly white, finely pulverulent* precipitate of *mercurous chloride* (calomel), Hg_2Cl_2. This is insoluble in cold hydrochloric and nitric acids, which, however, slowly dissolve it on boiling, hydrochloric acid converting it into metallic mercury and mercuric ion (together with chlorine ion), whilst nitric acid converts it completely into mercuric ion (together with chlorine and nitrate ions). *Aqua regia* and chlorine water readily dissolve mercurous chloride, converting it into mercuric chloride. *Ammonia* and *potassium and sodium hydroxides* decompose mercurous chloride, the first yielding a black mixture of very finely divided mercury with the so-called infusible white precipitate (See 74 5) The black precipitate produced by potassium and sodium hydroxides is a mixture of mercurous oxide with finely divided mercury and mercuric oxide (Barfoed).

7 Potassium iodide, added in small proportion to a solution of a mercurous salt, produces a green precipitate of mercurous iodide, Hg_2I_2, which is *soluble in excess of potassium iodide solution* as mercuric potassium iodide, with the separation of metallic mercury. Hence, on adding excess of potassium iodide, a grey precipitate of mercury is immediately produced

8. When a drop of a neutral or slightly acid solution of a mercurous salt is applied to **bright copper,** and the surface of the metal washed after some time, the spot, when gently rubbed with wool, paper, etc , appears *silvery-white and lustrous*. On heating the copper gently, the apparent silver plating disappears, owing to the volatilisation of the mercury. Solutions of mercurous salts behave towards metals in the same way as solutions of mercuric salts (*cf.* Sec. 74, 9).

9. **Stannous chloride,** when added *in very small proportion in very dilute solution* to the solutions of mercurous salts, gives a *white* precipitate of *mercurous chloride*. *On the addition of any considerable quantity of stannous chloride the white precipitate, which appears momentarily, changes into a grey mixture of mercurous chloride with finely divided mercury.* When an excess of stannous chloride is added the *grey precipitate* is converted into a black one of finely divided *metallic mercury*. This may be made to coalesce into globules of mercury by allowing the precipitate to subside, and, after decanting the supernatant liquid, boiling the residue with hydrochloric acid, to which a little more stannous chloride has been added (*cf.* also Sec 71, 6).

10. *Potassium chromate* produces in not too dilute solutions of mercurous salts a bright red precipitate of *basic mercurous chromate*, $3Hg_2CrO_4 + Hg_2O$, which dissolves with some difficulty in nitric acid.

11. A solution of *diphenylcarbazide* in alcohol gives a *bluish-violet coloration* with neutral or slightly acid solutions of mercurous salts This is a very sensitive reaction, which, however, is masked by copper ion and inhibited by zinc ion. (The reagent must be quite white; if not, it must be recrystallised from acetone).

12. When anhydrous mercurous compounds are **intimately mixed with anhydrous sodium carbonate,** and the mixture introduced into a glass tube closed by fusion at the lower end, covered with a layer of sodium carbonate, and **strongly heated,** there is invariably a decomposition in which metallic mercury is liberated. It is deposited as a grey *sublimate* above the place which was heated, and this may be seen with the aid of a lens or a microscope to be composed of globules of mercury. On rubbing the sublimate with a glass rod, the fine particles of mercury coalesce into larger globules. When a very small granule of iodine is placed close to the deposit, after cooling, and gentle heat is applied, the sublimate is converted into *mercuric iodide*. As a rule this is red at first and can then easily be seen, but sometimes it may be yellow at first and is then not so readily recognised. But if the tube is allowed to stand for some time the yellow iodide is transformed into the red modification. The conversion of mercury sublimate into an iodide deposit may also be effected by passing the tube containing the sublimate through a hole in cardboard and suspending it with its open end downwards in a small beaker containing iodine (Nega).

13. With regard to the *microchemical detection* of mercurous

compounds, see Haushofer, *Mikroskopische Reaktionen*, p. 111; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 116; Schoorl, *Zeitsch. anal. Chem.*, 47, 218.

SEC. 72.

(c) **Lead,** Pb, 207.20.

1. *Lead* is *divalent* and *tetravalent* in its compounds. Metallic lead is bluish-grey, lustrous when freshly cut, soft, readily fusible (at 327°), and volatilises at a white heat. Its specific gravity is 11.36. When fused on charcoal by means of the blowpipe it forms a deposit of yellow oxide on the charcoal. It is but little attacked by hydrochloric acid and moderately concentrated sulphuric acid, even on heating, but dilute nitric acid dissolves it readily, especially when hot.

2. *Lead oxide* (litharge), PbO, is a yellow or reddish-yellow powder, which appears brownish-red when hot; it is fusible at white heat. Lead hydroxide, $Pb(OH)_2$, is white; the plumbites with the anions PbO''_2 or $(HO)PbO'$ are derived from it. Both are dissolved by nitric and acetic acids. *Lead peroxide*, PbO_2, is brown; is converted by ignition into lead oxide, and is not soluble in hot nitric acid, but dissolves readily when a little sugar, alcohol, or hydrogen peroxide is added. The solution contains the ions of lead nitrate. *Lead sesquioxide*, Pb_2O_3, and *red lead*, Pb_3O_4, must be regarded as lead salts of *plumbic acid*, $Pb(OH)_4$, $PbO(O_2Pb)$, and $Pb(O_2Pb)_2$. The sesquioxide is yellow, and red lead is red. Nitric acid dissolves the lead cation from them, and leaves lead peroxide.

3. The salts which contain divalent lead are not volatile, and are usually colourless; the neutral salts soluble in water redden litmus in consequence of hydrolysis, and are decomposed on ignition. Of the insoluble salts only a few, *e.g.* lead carbonate, $PbCO_3$, are decomposed on ignition. Lead chloride, $PbCl_2$, when ignited in the presence of air, is partially volatilised, and leaves a residue of lead oxychloride.

4. **Hydrogen sulphide** and also **ammonium sulphide** produce a *black precipitate of lead sulphide*, PbS, *insoluble in cold dilute acids* and in *alkali, alkali sulphide*, and *potassium cyanide solutions. The precipitate is decomposed by hot nitric acid.* If the nitric acid is dilute the whole of the lead is dissolved, whilst sulphur separates, but if it is fuming acid the sulphur is also completely oxidised, and only insoluble lead sulphate is obtained: in the case of acid of

medium concentration, both processes occur, *i.e.* part of the lead is dissolved as lead nitrate, whilst the remainder separates as lead sulphate, together with the unoxidised sulphur. If a solution of a lead salt contains a large excess of a concentrated mineral acid, no precipitate is produced by hydrogen sulphide until after dilution with water, or until the acid has been partially neutralised with alkali hydroxide. The reaction $Pb^{\cdot\cdot} + H_2S \rightleftarrows PbS + 2H^{\cdot}$ thus only proceeds to a pronounced extent from left to right (practically complete precipitation of the lead sulphide) when the hydrogen ion concentration is small. If it is high the process is retarded or entirely inhibited. When a lead solution is treated with hydrogen sulphide in the presence of much free hydrochloric acid, a *red precipitate* of *lead sulphochloride*, Pb_2SCl_2, is sometimes obtained, but this is gradually converted by excess of hydrogen sulphide into black lead sulphide

5. *Ammonium thioacetate* produces in a cold hydrochloric acid solution of lead salts a red precipitate (sulphochloride), which, on heating, is completely converted into black lead sulphide

6. *Sodium thiosulphate* gives a white precipitate soluble in excess of the precipitant, with solutions of lead salts In the presence of free acid a black precipitate of lead sulphide is obtained on heating the liquid.

7. **Potassium and sodium hydroxides** and also **ammonia** produce *white precipitates* of *hydroxide* or *basic salts*, which are *insoluble* in *ammonia, but dissolve in potassium and sodium hydroxide solutions, with the formation of ions of alkali plumbite*, $Pb(ONa)_2$, or $Pb(OH)(ONa)$. Ammonia solution, free from carbonates, does not immediately produce a precipitate in solutions of lead acetate, owing to its forming soluble basic lead acetate.

Hydrogen peroxide, *hypochlorites*, and *persulphates* produce a precipitate of *lead peroxide* in *alkaline* solutions of lead salts

8. *Sodium carbonate* produces in the cold a white precipitate of neutral *lead carbonate*, and at boiling temperature one of slightly basic carbonate, which is insoluble in potassium cyanide solution, but not quite insoluble in excess of the precipitant.

9. **Hydrochloric acid** and **soluble chlorides** produce in *concentrated solutions a heavy white crystalline precipitate of lead chloride*, $PbCl_2$, which is *soluble in a large volume of water, especially on heating* This is converted by ammonia into lead oxychloride, $3PbO.PbCl_2.H_2O$, which is also a white powder, but is quite insoluble in water. Lead chloride is less soluble in dilute hydrochloric and nitric acids than

in water. It is more readily soluble in concentrated hydrochloric acid.

10. *Potassium iodide* gives a precipitate of *yellow lead iodide*, PbI_2, which is somewhat soluble in excess of potassium iodide solution.

11. **Sulphuric acid and sulphates** produce a *white precipitate of lead sulphate*, $PbSO_4$, which is *almost insoluble* in *water* and *dilute acids*. In the case of dilute solutions, especially such as contain much free acid, the precipitation only takes place after some time, often a considerable time. It is advisable to add a fairly large excess of dilute sulphuric acid. This increases the sensitiveness of the reaction, since lead sulphate is more insoluble in dilute sulphuric acid than in water. The best method of separating small amounts of lead sulphate is to evaporate the solution as far as possible, after the addition of the sulphuric acid (so as to eliminate the disturbing influence of volatile acids, *e.g.* nitric acid, upon the lead sulphate), and then to treat the residue with water, or better (when this is permissible), with alcohol. Lead sulphate is somewhat soluble in concentrated *nitric acid*; boiling concentrated *hydrochloric acid* dissolves it with some difficulty, whilst it dissolves more readily in *potassium hydroxide solution*. It also dissolves fairly easily in the solutions of some ammonium salts, notably those of *ammonium acetate* and *ammonium tartrate*, especially on moderate heating, owing to the formation of a complex anion; from these solutions it is re-precipitated by dilute sulphuric acid.

12. *Potassium chromate* produces a yellow precipitate of *lead chromate*, $PbCrO_4$, which is readily soluble in potassium and sodium hydroxide solutions, but dissolves with difficulty in dilute nitric acid, and is insoluble in ammonia solution.

13. An acetic acid solution of *tetramethyldiaminodiphenylmethane* gives with *lead peroxide* (but not with lead salts) an intense blue coloration (Trillat, *Compt. rend.*, **136**, 1205; *Chem. Zentr.*, 1903, II., 68). This is a very sensitive reaction. The substance is calcined, the ash oxidised with sodium hypochlorite and treated with water, and the filtrate heated and tested with the reagent.

14. Lead compounds, when mixed with **sodium carbonate** in a hollow on charcoal and exposed to the **reducing flame of the blow-pipe**, readily yield soft, malleable **metal particles.** Simultaneously the surface of the charcoal becomes coated with a *yellow film of lead oxide*. The reduction may also be easily effected on *charcoal sticks* (p. 88).

15. The *deposit of metallic lead* obtained, as described on p. 89, is black, extending into a brown film, the *oxide* deposit is pale ochre yellow, the *iodide* deposit deep yellow to lemon-yellow, whilst the *sulphide* deposit changes from brownish-red to black, and is not removed by ammonium sulphide (Bunsen).

16. With regard to the *microchemical detection* of lead, see Haushofer, *Mikroskopische Reaktionen*, p. 25, Behrens-Kley, *Mikrochemische Analyse*, 3rd ed, p 91; Schoorl, *Zeitsch. anal. Chem*, **47**, 211, 211, 710, 715, 749; **48**, 669.

SEC. 73.

Summary and Remarks on Group V. (Div I.).

The members of the first division of the fifth group are differentiated most distinctly by means of their chlorides, the different behaviour of which towards water and ammonia solution enables them to be both detected and separated. Thus, if the precipitate containing the three chlorides is treated with a somewhat large amount of water, or is washed repeatedly on the filter with boiling water, the lead chloride dissolves, whilst silver chloride and mercurous chloride remain undissolved. The lead ion may then be easily detected by means of sulphuric acid in the aqueous solution of lead chloride On then treating the silver chloride and mercurous chloride with ammonia solution, the mercurous chloride is converted into the black precipitate (described more fully above, Sec. 71, end of 6), which is insoluble in excess of ammonia solution, whilst the silver chloride dissolves, and may be re-precipitated from this solution by adding nitric acid[1] (In the case of small amounts it is advisable first of all to evaporate most of the ammonia). If, however, the chlorides were precipitated from a solution which contained much mercurous ion and only a little silver ion, the silver chloride cannot be completely extracted from them by means of ammonia solution, and in presence of a very large excess of mercurous chloride it is possible for the whole of the silver chloride to be retained by the black mercury precipitate (Moeck[2]). When, therefore, much mercury is present and no silver ion has been found in the filtrate, the black mercury precipitate should be ignited in a porcelain crucible in a fume cupboard, until the whole of the mercury has volatilised, and the residue heated with a few crystals of oxalic acid until they too have volatilised, after which the residue is treated with hot nitric acid, and the solution slightly diluted with water, and tested for silver ion with hydrochloric acid.

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[1] If the lead chloride has previously been extracted with hot water, but without dissolving the whole of it, the ammoniacal solution will often show a white turbidity (*cf.* Sec. 72, 9). In such cases the lead oxychloride may be filtered off, and the silver ion detected in the filtrate.

[2] According to N. v Zweigbergk, this is due to the fact that silver chloride in ammoniacal solution forms a silver amalgam with mercury. Hence Zweigbergk recommends oxidation by Thiel's method (see next paragraph) or by means of sodium hypochlorite and nitric acid (*Chem. Zentr*, 1916, I 489).

For the detection of silver in the presence of mercury, the chlorides may also be treated with bromine water, which dissolves the mercurous chloride as a mercuric compound, whilst the silver chloride is left (Thiel, *Chem. Zentr*, 1905, I., 105)

For the separation of silver ion from lead ion, or for the detection of a small quantity of silver ion in the presence of such lead ion, the following methods may be used: (*a*) A little nitric acid is added to the solution and then a mixture of equal parts of ammonia solution and hydrogen peroxide, together with some ammonium carbonate Lead ion then separates from the ammoniacal liquid as a reddish-yellow precipitate, consisting of a compound of peroxide and oxide, whilst silver remains in solution On filtering off the precipitate, acidifying the filtrate with nitric acid, and adding a little hydrochloric acid, the silver ion separates as silver chloride (P Jannasch) (*b*) The solution containing the lead and silver ions is heated with a little nitric acid, treated with a slight excess of potassium chromate or dichromate, again heated, and, after the addition of an excess of dilute ammonia solution, once more heated for some time, and filtered Lead chromate will be left on the filter, whilst the ammoniacal filtrate will contain the silver chromate. On then acidifying the filtrate with nitric acid and adding a little hydrochloric acid, the silver ion will be precipitated as silver chloride (P. Jannasch[1])

Second Division

Of the Members of the Fifth Group of frequent occurrence.

Ions not precipitated by hydrochloric acid.

SEC. 74.

(a) **Mercury** (as **Mercuric ion,** $Hg^{\cdot\cdot}$).

1. *Mercuric oxide*, HgO, is either bright red and crystalline, becoming a dull yellowish-red powder when rubbed, or, as pre-

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[1] For further methods of detecting a small amount of silver ion in the presence of much lead ion, see Krutwig, *Zeitsch. anal. Chem*, **22**, 428; Johnstone, *Chem. Zentr.*, 1890, I, 298.

cipitated from a solution of mercuric nitrate or chloride, is a yellow powder. Mercuric oxide is not absolutely insoluble in water; exposed to sunlight it gradually turns grey; when heated, it transitorily becomes darker, and is decomposed at a low ignition temperature into oxygen and mercury. It is readily dissolved by hydrochloric and nitric acids.

2. Most of the *mercuric salts* are colourless. When ignited they volatilise, being meanwhile decomposed, with the exception of mercuric chloride (corrosive sublimate), bromide, and iodide, which are not decomposed. Mercuric chloride also volatilises with the steam when its solution is boiled. The salts are very poisonous. The neutral salts soluble in water redden litmus in consequence of hydrolysis. Mercuric nitrate and sulphate are decomposed, when treated with a large amount of water, into soluble acid salts and insoluble basic salts.

3. When **hydrogen sulphide** or **ammonium sulphide** is added in very small proportion to solutions of mercuric salts, and the liquid shaken, an absolutely *white precipitate* is obtained; a somewhat larger addition causes the precipitate to be *yellow*, *orange*, or *brownish-red;* whilst an excess of the reagent produces an *absolutely black precipitate of mercuric sulphide*, HgS. This change in the colour of the precipitate, according to the quantity of hydrogen sulphide added, distinguishes the mercuric compounds from all other substances. It depends upon the fact that a *white double compound* of *mercuric sulphide with undecomposed mercuric salt, e.g.* $2HgS + HgCl_2$, is first formed, and that this changes into yellow and brown compounds richer in sulphide, and finally into pure sulphide. Only *traces* of mercuric sulphide are dissolved by *ammonium sulphide solution*, least being dissolved when it is digested with hot yellow ammonium sulphide. Potassium hydroxide and potassium cyanide solutions do not dissolve mercuric sulphide. *Potassium and sodium sulphide* solutions dissolve it *completely* in the presence of a little potassium or sodium hydroxide. (Distinction from silver, lead, bismuth, and copper ions.) Ammonium chloride precipitates mercuric sulphide from its potassium or sodium sulphide solution. Potassium thiocarbonate solution[1] dissolves mercuric sulphide (distinction from silver, lead, bismuth, copper, and cadmium ions),[2] and it is re-precipitated from its solution therein by carbon dioxide.

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[1] See Sec. 59, 13.

[2] Cadmium sulphide retains a little mercuric sulphide (*Zeitsch. anal Chem.*, **26**, 17).

(Distinction from palladium ion. Rosenbladt.) In the absence of chlorides mercuric sulphide is completely insoluble in ***dilute nitric acid***, even on boiling. The long-continued action of hot concentrated nitric acid converts it into the white compound, $2HgS+Hg(NO_3)_2$, and finally dissolves it as nitrate.

Concentrated hot hydrochloric acid dissolves it fairly easily, the cold acid with more difficulty; it is insoluble, or nearly so, in cold dilute hydrochloric acid, but slightly soluble in the boiling dilute acid. *Aqua regia* or hydrochloric acid and potassium chlorate readily decompose and dissolve mercuric sulphide. If a solution of a mercuric salt contains a large excess of concentrated mineral acid, a precipitate is not produced by hydrogen sulphide until the liquid has been diluted with water.

Ammonium thioacetate, added in the cold to hydrochloric acid solutions of mercuric salts, produces a red precipitate (mercuric sulphochloride), whilst on heating it gives a black precipitate (mercuric sulphide).

Sodium thiosulphate produces in a boiling slightly acid solution a white precipitate, which changes to orange and finally to black. Any material excess of acid influences the reaction, so that small amounts of mercuric precipitate may be completely masked by the separation of sulphur.

4. **Potassium and sodium hydroxides,** when added in *insufficient quantity* to neutral or slightly acid solutions of mercuric salts,[1] produce a *reddish-brown* precipitate; if added *in excess*, a *yellow* precipitate. The former is a basic salt and the yellow precipitate *mercuric oxide*. The precipitate is not soluble in excess of the precipitant. In the case of *very acid solutions* there is either no precipitation or only a slight one; in the presence of ammonium salts neither red-brown nor yellow precipitates are produced, but white ones. That which is precipitated from mercuric chloride solution in the presence of excess of ammonia approximates in composition to the precipitate described in 5.

5. **Ammonia** produces white precipitates very similar to those produced by potassium and sodium hydroxides in the presence of ammonium chloride; for example, it precipitates the so-called infusible white precipitate, mercuric ammonium chloride, $(NH_2)HgCl$, from mercuric chloride solution. If the solution of the *mercuric* salt contains much free acid, no precipitate is produced by ammonia.

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[1] With the exception of mercuric cyanide, which forms soluble complex salts, *e.g.* $[Hg(CN)_2Cl]K$ or $K_2Hg(CN)_4$.

The white precipitates do not dissolve in ammonia solution, but are readily soluble in hydrochloric acid (*cf* also Sec 30, 11)

6. **Stannous chloride solution,** when added in small proportion to mercuric chloride solution, or, in the presence of hydrochloric acid, to a solution of another mercuric salt, produces a precipitate of *mercurous chloride*, $2HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4$. If a large amount of the reagent is added, the mercurous chloride first precipitated is reduced to metallic mercury, $Hg_2Cl_2+SnCl_2=2Hg+SnCl_4$ Hence the precipitate, which at first is white, becomes grey, and after subsiding may be made to coalesce into globules of mercury by boiling it with hydrochloric acid and a little stannous chloride

Other reducing agents (*phosphorous acid,*[1] *hypophosphorous acid*, and *hydrogen peroxide*[2]) also effect a separation in the presence of chlorine ion of mercurous chloride from solutions of mercuric salts.

Hydroxylamine chloride and *hydrazine sulphate* liberate metallic mercury from an ammoniacal solution of a mercuric salt which has been treated with tartaric acid.[3]

7. **Potassium iodide** precipitates red *mercuric iodide*, which dissolves in excess of the precipitant as mercuric potassium iodide In the presence of potassium hydroxide, ammonia produces a yellow precipitate in this solution (*cf* Sec. 30, 10) Klein, and also Denigès and Moore, recommend this reaction for the detection of small amounts of mercury (*Zeitsch. anal. Chem.*, **29**, 186, and *Chem. Zeit.*, **20**; 70 ; *Chem. Zentr*, 1911, II., 989).

8 *Mercuric salts* behave towards diphenylcarbazide in the same way as mercurous salts.

9. Metals which are more electropositive than mercury (copper, zinc, iron, aluminium) liberate from solutions of mercuric salts (as also from those of mercurous salts) metallic mercury, which, when the quantity is in any way considerable, may be easily identified upon copper, as described in Sec 71, 8.

In this process *aluminium* forms an amalgam, which on exposure to the air, becomes oxidised, with the formation of alumina. The mercury amalgamates with more aluminium, and so causes the formation of more alumina, which thus, as it were, develops from the aluminium. This is a very sensitive reaction, which is also given by metallic mercury.

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[1] C. v. Uslar, *Zeitsch. anal. Chem.*, **34**, 391.

[2] Vanino and Treubert, *Ber.*, **30**, 2001 ; **31**, 129.

[3] Jannasch, *Ibid.*, **31**, 2377 ; **37**, 2219

This method of separating mercury by the use of finely divided metal (brass wool, etc.) is also particularly applicable to the detection of minute quantities of mercury, especially in the examination of urine (which must be rendered slightly acid) and in toxicological cases. Instead of this method electrolytic separation may also be used, a current derived from an outside source being conducted into the liquid, or a small element being formed which produces the current in the liquid itself. This element may be composed, *e.g.* of platinum foil and tin foil, the ends of which outside the liquid are in contact, whilst the free ends are immersed in the liquid which is to be tested for mercury. Whatever method is used, the metal upon which the mercury has been deposited is carefully washed with water (also with alcohol and ether in the absence of organic substances), then dried by means of filter paper, and finally heated in a clean dry tube, a portion of which has been drawn out into a capillary tube. In this way sublimates of mercury are obtained, which, if very minute so that they cannot easily be seen, may be identified more certainly by conversion into iodide (See 71, 12). (For details of the method, reference may be made to the general index of the *Zeitsch anal. Chem*) It need only be mentioned here that in the case of turbid urine the mercury may be present in the deposit (with precipitated albumin), and that the test must be applied, therefore, to the unfiltered urine.

For the precipitation of very small quantities of mercury by a method based upon another principle, see Raaschou, *Zeitsch. anal. Chem.*, **49**, 172

10. Solid mercuric compounds behave like mercurous compounds when mixed with dry *sodium carbonate* and heated in a glass tube (Sec. 71, 12).

11 When substances containing mercury are heated with *alkali formate*, hydrogen containing mercury vapour is produced. When this is ignited and the flame directed against an unglazed porcelain plate, a black stain of mercury is formed (Vournasos, *Compt. Rend.*, **150**, 922). This is a very sensitive reaction. In the presence of nitrates violent explosions may occur.

12 For the *microchemical detection* of mercuric compounds, see Haushofer, *Mikroskopische Reaktionen*, p. 112, Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 118; Schoorl, *Zeitsch. anal. Chem*, **47**, 218, 221; Emich, *Ibid.*, **54**, 500.

SEC. 75.

(b) Copper, Cu, 63·57.

1 *Copper* is *mono-* and *divalent*. Metallic copper has a characteristic red colour and pronounced lustre, and is moderately hard, and ductile; its specific gravity is 8·94. It melts with some difficulty

at 1084° ; in the air (owing to absorption of oxygen) at 1065° ; on contact with air and water it becomes coated with green basic carbonate, and on ignition in the air, with cuprous and cupric oxides. Copper is insoluble, or nearly so, in even boiling hydrochloric and dilute sulphuric acids in the absence of air, but dissolves readily in nitric acid, with the formation of nitric oxide, $3Cu+8HNO_3 = 3Cu(NO_3)_2+2NO+4H_2O$. Concentrated sulphuric acid dissolves copper as cupric sulphate, with the evolution of sulphur dioxide.

2. *Cuprous oxide*, Cu_2O, is red, the so-called cuprous hydroxide yellow;[1] both are converted into cupric oxide when ignited in the air. The cuprous halogenides are sparingly soluble and stable, the rest of the cuprous salts are unstable. On treating cuprous oxide with dilute sulphuric acid, metallic copper separates, whilst cupric sulphate dissolves; when treated with hydrochloric acid, cuprous oxide yields white cuprous chloride, which dissolves in an excess of the acid, but is re-precipitated from this solution by the addition of water. Cuprous chloride is also soluble in alkali chloride solution. Cuprous oxide and the corresponding cuprous salts are soluble in ammonia solution.

3. *Cupric oxide* (copper oxide), CuO, is a black powder, which can be heated to redness without decomposition. When strongly ignited, however, it loses oxygen and is partially converted into cuprous oxide. *Cupric hydroxide*, $Cu(OH)_2$, is light blue. Both oxide and hydroxide are readily soluble in hydrochloric, sulphuric, and nitric acids.

4. Of the neutral *cupric salts* many are soluble in water, and these redden litmus, owing to hydrolysis. The cupric salts of volatile acids are decomposed when gently ignited, with the exception of copper sulphate (blue vitriol), which can resist a somewhat higher temperature. Most of the cupric salts are colourless in the anhydrous condition, but blue or green when hydrated. Their solutions are also usually blue, even when considerably diluted. Cupric chloride in concentrated solution or in presence of excess of hydrochloric acid is green (the undissociated chloride is green, the cupric ion blue).

5. **Hydrogen sulphide** and **ammonium sulphide** produce in *alkaline, neutral, and acid solutions a brownish-black precipitate of cupric sulphide*, CuS (usually mixed with cuprous sulphide and sulphur). This precipitate does *not dissolve either in dilute acids*,

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[1] The existence of a true hydroxide is doubtful. Presumably the yellow substance is hydrated colloidal cuprous oxide.

(or in acidified alkali chloride solutions—distinction from cadmium, Cushman[1]), or *in alkali hydroxides.* Solutions of *potassium* or *sodium sulphide*, free from polysulphides, dissolve sulphur, but dissolve little, if any, *cupric sulphide*, even on heating; the precipitate is appreciably soluble, however, in yellow potassium or sodium sulphide solution (containing polysulphides) even in the cold (A. Rossing, *Zeitsch. anal. Chem.*, **41**, 1). In *ammonium sulphide solution*, however, cupric sulphide is somewhat more soluble, especially when the ammonium sulphide is very yellow and is used hot; hence this reagent *is not well suited* for the separation of cupric sulphide from the sulphides of Group VI. Cupric sulphide is *readily* decomposed and *dissolved* by boiling *nitric acid*, but not by boiling dilute sulphuric acid. *Potassium cyanide solution* dissolves freshly precipitated cupric sulphide readily and completely. If a copper solution contains an excess of a concentrated mineral acid, no precipitate is obtained until after diluting the liquid with water. Part of the cupric sulphide separates in colloidal form from a neutral solution, so that it cannot easily be filtered. The addition of acid causes it to flocculate. *Ammonium thioacetate* produces a partial precipitation of cupric sulphide in cold acid solutions of cupric salts, and complete precipitation in hot solutions. *Sodium thiosulphate* decolorises neutral or acid solutions of cupric salts, and gives a reddish-brown precipitate (subsequently becoming black) of cuprous sulphide mixed with sulphur. (Distinction from cadmium ion.)

6. *Acetylene* precipitates reddish-brown flocculent *cuprous* acetylide, $C_2Cu_2.H_2O$, from ammoniacal or tartaric acid solutions of copper salts which have been reduced with hydroxylamine (and thus contain cuprous ion). This affords a means of separating copper ion from many other metal ions (H. Erdmann and Makowka, *Zeitsch. anal. Chem.*, **46**, 128). The acetylene must be used in the purified form as gas after washing with lead acetate solution, or in aqueous solution prepared from the purified gas. Waegner (*Zeitsch. anal. Chem.*, **44**, 565) recommends the use of a solution of acetylene in acetone. H. G. Soderbaum (*Ibid.*, 561) recommends precipitation of copper ion from an unreduced solution by means of acetylene gas, as a means of separating it from many other metals. In this method cupric acetylide is precipitated.

7. **Potassium or sodium hydroxide** produces a *voluminous light blue precipitate of cupric hydroxide*, $Cu(OH)_2$. When left in contact with excess of the precipitant, this loses its water completely (more

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[1] *Zeitsch. anal. Chem.*, **34**, 368.

rapidly on heating), and changes into blue-black cupric oxide. When a *large excess* of a concentrated solution of potassium or sodium hydroxide is present, the light blue cupric hydroxide dissolves, forming a blue solution (or colloidal suspension).

8. **Sodium or potassium carbonate** produces in solutions of cupric salts greenish-blue precipitates of *basic carbonates* of varying composition, which on standing in contact with excess of the precipitant change into the crystalline salt $3CuCO_3.3Cu(OH)_2.H_2O$. These precipitates dissolve in ammonia solution to form an azure blue solution, but give a colourless solution with potassium cyanide. When boiled, they lose carbon dioxide and become brownish-black.

Notes to 7 and 8.—The presence of ammonium salts prevents or affects the precipitation by the hydroxides or carbonates of potassium or sodium (see 9). Copper forms complex anions with many organic substances, so that the precipitation by sodium hydroxide or carbonate is prevented. Thus, in the presence of tartaric acid and other non-volatile organic acids, deep blue solutions but no precipitates are obtained. In the presence of sugar and similar substances, alkali hydroxides produce precipitates which dissolve in excess of the precipitant; the alkali carbonates, however, give permanent precipitates.

9. **Ammonia,** when added *in very small proportion* to a solution of a neutral copper salt, produces a *greenish-blue precipitate of cupric hydroxide*, or a basic cupric salt; *on adding more ammonia solution, this precipitate dissolves easily and completely to form an azure blue liquid.* This depends upon the fact that complex cupric ammonia cations of varying composition, $Cu^{\cdot\cdot}(NH_3)_n$, are formed, the hydroxides or salts of which are soluble in water.

If ammonium salts or free acids are present, no precipitation, even a transitory one, will be produced by ammonia, but the solution will immediately become dark blue.

The blue colour of the solution is still visible after very great dilution, so that it affords a means of detecting minute quantities of cupric ion.

Potassium or sodium hydroxide produces a precipitate of blue cupric hydroxide in such blue solution after a considerable time in the cold, but on boiling the liquid for some time the whole of the copper is precipitated as brownish-black cupric oxide.

Ammonium carbonate behaves towards solutions of cupri salts in the same way as ammonia.

Very small quantities of cupric ions do not give the blue coloratio with ammonia in excess, but on shaking the solution with a few drops of *phenol* solution a blue coloration will be produced after standing for some time (15 minutes to 1 hour) (Jaworowski, *Chem. Zentr*, 1896, I., 770).[1]

10. **Potassium ferrocyanide** produces *a reddish-brown precipitate of cupric ferrocyanide*, $Cu_2Fe(CN)_6$, in moderately dilute solutions, but only a red coloration in very dilute solutions. The precipitate is insoluble in dilute acids, but is decomposed by potassium or sodium hydroxide.

11. **Potassium thiocyanate** produces a black precipitate of *cupric thiocyanate* in solutions of cupric salts, $Cu^{\cdot\cdot}+2CNS'=Cu(CNS)_2$; for example, $CuSO_4+2KCNS=Cu(CNS)_2+K_2SO_4$. The precipitate is not quite insoluble, so that complete precipitation of the copper does not take place. In somewhat dilute or acid solutions there is frequently only a dark coloration. *On adding (preferably before the addition of potassium thiocyanate) a reducing agent such as sulphur dioxide, sodium sulphite and hydrochloric acid, or a salt of hydroxylamine or of hydrazine,*[2] *the copper is precipitated as reddish-white to white cuprous thiocyanate*, which is almost completely insoluble in water and dilute acids:

$$2Cu^{\cdot\cdot}+2CNS'+SO_2+2H_2O=2CuCNS+4H^{\cdot}+SO''_4$$

for example

$$2CuSO_4+SO_2+2KCNS+2H_2O=2CuCNS+K_2SO_4+2H_2SO_4$$

12. *Potassium iodide* precipitates white cuprous iodide, Cu_2I_2, whilst iodine is also liberated, so that the precipitate appears green to reddish-yellow. On adding a reducing agent (sulphur dioxide,

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[1] For the detection of very small quantities of copper, Wildenstein, *Zeitsch. anal. Chem.*, **2**, 9; Bellamy, *Ibid.*, **9**, 382; Bradley, *Chem. Zentr.*, 1906, II., 1873, recommend hæmatoxylin; Schaer, *Zeitsch. anal. Chem.*, **9**, 100; Schonn, *Ibid.*, **9**, 210; Purgotti, *Ibid.*, **18**, 476, recommends guaiacum tincture and Prussian blue; Von Knorre, *Ibid.*, **28**, 231, α-nitroso-β-naphthol; Baudisch and Rothschild, *Ber.*, **48**, 1660, *o*-nitrosonaphthol; A. Bach, *Chem. Zentr.*, 1899, I., 639, formaldoxime; Delépine, *Ibid.*, 1908, II., 261, dialkylthiosulphocarbamic acid; Lyle, Curtman, and Marshall, *Ibid.*, 1915, II., 632, α-amino-*n*-caproic acid; R. Ulenhuth, *Ibid.*, 1910, II., 914; also Malatesta and Di Nola, *Ibid.*, 1914, I., 820, 1.2-diamino-anthraquinone-3-sulphonic acid; Mayer and Schramm, *Zeitsch. anal. Chem.*, **56**, 129, sodium hydrogen carbonate and hydrogen peroxide; E. Knecht, *Ber.*, **41**, 498, titanium sesquisulphate; Schander, *Chem. Zentr.*, 1905, I., 267, calls attention to the fact that beans and fragments of potatoes can absorb copper from very dilute solutions, whilst Ebert, *Zeitsch. anal. Chem.*, **49**, 47, shows that this is also the case with cotton-wool.

[2] Salts of hydrazine and hydroxylamine give, in the presence of alkali, a precipitate of cuprous oxide (Knoevenagel and Ebler, *Ber.*, **35**, 3065.

sodium sulphite, ferrous sulphate, phenylhydrazine) no free iodine is obtained, but only the white precipitate of cuprous iodide.

In the case of very dilute solutions a yellow coloration is still perceptible on the addition of potassium iodide (Thoms, *Pharm. Zentralhalle*, **31**, 30).

13. *Potassium bromide solution*, when treated with concentrated sulphuric acid, on to which a small quantity of a solution of a cupric salt is then poured, at first produces a bluish-red zone at the point of contact. On shaking the liquid, the colour of the whole solution becomes red. (In the presence of any considerable amount of cupric ion a black precipitate is produced by the potassium bromide and concentrated sulphuric acid.) The red coloration disappears on the addition of water. This reaction is very sensitive, and enables cupric ion to be detected in the presence of the salts of other metals (Denigès). Stannous chloride or bromide inhibit the reaction by causing reduction of the cupric ion to cuprous ion (Viard, *Compt. rend.*, **135**, 168, 242; *Chem. Zentr.*, 1902, II., 563, 630) According to Sabatier, the coloration is due to a compound $CuBr_2.HBr\ 2H_2O$. On adding sulphur dioxide solution in not too great proportion to the dark bluish-red liquid a precipitate of white cuprous bromide is obtained.[1]

14. *Diphenylcarbazide* in alcoholic solution (1 : 100) produces an intense violet coloration in neutral or only slightly acid solutions This is a very sensitive reaction (Cazeneuve, *Zeitsch. anal. Chem*, **41**, 568).

15. On shaking a neutral or slightly acid solution of a cupric salt with a petroleum spirit solution of *naphthenic acids*, the layer of petroleum spirit is coloured green This is a very sensitive reaction (Charitschkoff, *Chem. Zeit*, **34**, 479; and *Chem. Zentr.*, 1909, I., 1947; and 1910, I., 2036; *cf.* also *Zeitsch. anal. Chem.* **58**, 127).

16. *Hypophosphorous acid* produces in solutions of cupric salts in the cold a yellow precipitate of *cuprous hydride*, CuH, which, on heating, is decomposed into its constituents. Hence, from a boiling solution the reagent precipitates copper directly. (Distinction from zinc and cadmium ions. F. Mawrow and W. Muthmann, *Zeitsch. anorg. Chem*, **11**, 268.)

17. *Oxalic acid* gives a bluish-white precipitate of *cupric oxalate* with neutral or slightly acid solutions of cupric salts. The boiling

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[1] Concentrated hydrobromic acid acts in the same way as potassium bromide and sulphuric acid (Endemann and Prochazka, *Zeitsch. anal. Chem.*, **21**, 265).

solution is treated with a moderate excess of solid oxalic acid. (Distinction from cadmium ion.)

18. **Metallic iron,** *when brought into contact with solutions of cupric salts, becomes coated with a reddish deposit of metallic copper,* almost instantaneously if the solution is concentrated, and after a considerable time if it is very dilute. The presence of a little free acid promotes the reaction, which, however, may be masked by the presence of many other metals which are also precipitated by iron. Copper is also precipitated as a red deposit upon other more electropositive metals, *e g* zinc In like manner, copper may be electrolytically deposited upon a cathode.

A simple device for this purpose may be made by binding together a strip of platinum foil and a strip of zinc or tin foil at their upper ends, introducing a section of cork and binding them also at this place. The strips are arranged almost parallel to each other, and are introduced into the slightly acidified copper solution in such a way that the unbound portion is not immersed The copper is then deposited (in the case of very dilute solutions not until after about twelve hours) mainly upon the platinum, the surface of which becomes copper-red to black The advantage of this deposition of copper upon the platinum is that the copper may be readily dissolved in nitric acid and further tests applied to the solution. For this purpose the liquid is evaporated almost to dryness, a few drops of water added, and then a drop of potassium ferrocyanide solution. Traces of copper deposited on iron or platinum may be identified by moistening them with hydrochloric acid and testing them as in 21. Salet recommends that the hydrochloric acid should be applied by immersing in it a bundle of fine platinum wires, and heating this in a flame beneath the iron rod or platinum strip This materially increases the sensitiveness of the reaction.

19 With regard to the detection of cupric ion, even in the presence of other cations, by means of its *absorption spectrum* in the presence of *alkanet tincture*, see Formáneck, *Zeitsch. anal. Chem.*, 39, 119, 131, *et seq*

20 On mixing copper compounds with **sodium carbonate** in a hollow on charcoal and exposing the mixture to the **inner blowpipe flame,** *metallic copper* is obtained without a simultaneous deposit of oxide; the reaction also takes place very well on *charcoal sticks* (p 88). The reduced copper may best be recognised by grinding the mass, including the surrounding portions of charcoal, with water in a small mortar, and washing away the charcoal powder. The copper-red particles of metal are then left in the residue.

21. If copper, an alloy containing copper, a trace of a copper salt, or a loop of platinum wire, which has been dipped into even a

very dilute solution of a copper salt, is introduced into the **fusion area of a gas flame,** or into the inner blowpipe flame, a fine emerald-green coloration is imparted to the upper or outer flame. The addition of *hydrochloric acid* to the substance or solution intensifies the delicacy of this extremely sensitive reaction The flame then appears azure blue on the exterior. Since the colour of the flame varies somewhat according to the conditions or the nature of the anion present, the spectroscopic appearance is also somewhat variable

22. **Alkali phosphate** and **borax** dissolve copper readily in the outer gas flame. The beads appear *green while hot* and *blue when cold.* In the inner flame, if the amount of copper is not too great, they appear colourless, and become *red and opaque on cooling.* In the lower reducing area of the Bunsen flame the beads readily become reddish-brown on the addition of a little *tin oxide*, owing to the formation of *cuprous oxide*, but do not by themselves show this coloration. If the beads are brought alternately into the lower oxidising and reducing area they become ruby-red and transparent.

23. For the *microchemical detection* of copper ion, see Haushofer, *Mikroskopische Reaktionen*, p. 87 ; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 65 ; Schoorl, *Zeitsch anal. Chem.*, **47**, 710, Pozzi-Escot, *Chem. Zentr.*, 1900, I , 399, and 1907, II., 481.

SEC. 76.

(c) **Bismuth,** Bi, 208.0.

1. *Bismuth* is *trivalent.* Metallic bismuth resembles tin with a reddish tint ; it has a moderate lustre, is fairly hard and brittle and has a specific gravity of 9·78. It does not change in the air at the ordinary temperature, melts at 269°, and when fused on charcoal forms a deposit of yellow oxide. It is readily soluble in nitric acid, hardly soluble in hydrochloric acid, and insoluble in dilute sulphuric acid. Concentrated sulphuric acid converts it into bismuth sulphate, with the liberation of sulphur dioxide.

2. *Bismuth oxide*, Bi_2O_3, is a yellow powder, which transitorily becomes dark yellow when heated, and melts at a red heat. *Bismuth hydroxide*, $Bi(OH)_3$, is white ; bismuthyl hydroxide, BiO.OH, is white or yellow (see 5). The oxide and hydroxides are readily soluble in hydrochloric, sulphuric, and nitric acids. When fused with potassium cyanide they yield the metal. (Other compounds of bismuth and oxygen are also known, some containing less oxygen, which, according to some authorities, are mixtures of bismuth and bismuth oxide, and

others with more oxygen, but the nature of these has not yet been definitely determined. They are all converted into oxide when heated in the air, and into nitrate when heated with nitric acid.)

3. Bismuth forms *two series of salts*, viz. the normal salts of the trivalent bismuth ion, $Bi^{\cdot\cdot\cdot}$, and the salt of the monovalent bismuthyl ion, $BiO^{\cdot}$. Nearly all the bismuth salts are non-volatile; the salts of volatile acids are decomposed on ignition; bismuth chloride, $BiCl_3$, is volatile at a moderate heat. The bismuth salts are colourless or white, except when the anion causes them to be coloured. Some of the salts of bismuth ion, $Bi^{\cdot\cdot\cdot}$, are insoluble in water, others are soluble in a little water. The latter, owing to the extremely weak basic character of the $Bi^{\cdot\cdot\cdot}$ ion, undergo hydrolysis to a pronounced extent, as do also the salts of the $BiO^{\cdot}$ ion; their solutions redden litmus. They are decomposed by **any considerable amount of water** into bismuthyl salts, which subside as white precipitates, and free acid, which then checks the hydrolysis of the remainder of the bismuth salt; in the presence of a large amount of water, complete precipitation takes place: $Bi^{\cdot\cdot\cdot} + H_2O = BiO^{\cdot} + 2H^{\cdot}$. Under certain conditions, still more basic compounds are formed, *e.g.* $(BiO)_2(OH)(NO_3)$. Acid dissolves the precipitates thus formed; or, if added beforehand, prevents their formation.

In the case of *bismuth chloride* the separation as bismuthyl compound takes place particularly readily, so that, for example, bismuth nitrate solutions, which contain so much free acid that they remain clear, may give a precipitate of bismuthyl chloride, on the addition of a chloride, or even of hydrochloric acid. *This precipitation of a bismuthyl salt by means of water is a particularly characteristic reaction of bismuth ion.*

4. **Hydrogen sulphide** and **ammonium sulphide** produce in *neutral* and *acid solutions* a *black precipitate of bismuth sulphide*, Bi_2S_3, insoluble in dilute acids and alkali and potassium cyanide solutions. It is readily decomposed and dissolved by boiling nitric acid. Bismuth solutions, which contain a very considerable excess of hydrochloric acid or nitric acid, only give a precipitate with hydrogen sulphide after dilution with water. Bismuth sulphide precipitated from *acid* solution is insoluble in alkali sulphide solutions; but that precipitated by means of *alkali sulphide*, or from an *alkaline solution*, is soluble to a considerable extent in excess of potassium or sodium sulphide solution.

Ammonium thioacetate produces a precipitate of bismuth sulphide in acid solutions of bismuth salts, partially in the cold and completely on heating. *Sodium thiosulphate*, when added to a not too acid solution of a bismuth salt, produces first a yellow coloration and then a precipitate of bismuth sulphide:

$$2Bi^{\cdot\cdot\cdot}+3S_2O''_3+3H_2O=Bi_2S_3+6H^{\cdot}+3SO''_4$$

for example

$$2Bi(NO_3)_3+3Na_2S_2O_3+3H_2O=Bi_2S_3+6NaNO_3+3H_2SO_4$$

5. **Potassium** and **sodium hydroxides** and also **ammonia** precipitate *hydroxide* (mixed with basic or bismuthyl salt). The bismuth hydroxide is somewhat soluble in concentrated solutions of potassium and sodium hydroxide, especially on heating, but the precipitation from a dilute solution is complete in the cold. If the precipitation has been made by means of a fairly concentrated solution of potassium or sodium hydroxide, the precipitate will become *yellow* on standing, and more rapidly if heated in the liquid from which it was precipitated. The *yellow coloration* is produced with *most certainty* after the addition of a little *hydrogen peroxide* or *chlorine water*. According to Rupp, however, the yellow substance is not bismuth peroxide, since it does not liberate iodine, but only BiO.OH (*Zeitsch. anal. Chem.*, **42**, 732). Hanus and Kallauner (*Zeitsch. anorg. Chem.*, **70**, 232, *Chem. Zentr.*, 1911, I., 1542) have found that ammoniacal hydrogen peroxide or alkaline sodium peroxide produces yellow precipitates in the cold and brown precipitates on heating, which liberate iodine from an acid solution of potassium iodide.[1]

6. **Sodium carbonate** and **ammonium carbonate** precipitate *basic bismuth carbonate* of variable composition, *e.g.* bismuthyl carbonate, $(BiO)_2CO_3$, in the form of a voluminous white precipitate insoluble in excess of the precipitant and in potassium cyanide solution. Heat promotes the precipitation.

7. **Potassium iodide** produces in a concentrated sufficiently acid solution a *black precipitate* of *bismuth iodide*, BiI_3, which dissolves as *orange-coloured potassium bismuth iodide in excess of potassium iodide solution*. More dilute and less acid solutions yield an orange-coloured precipitate of bismuthyl iodide, especially when heated. The solution of potassium bismuth iodide is decomposed on dilution with water; if very little water is added black bismuth iodide separates, whilst on the addition of much water the precipitate consists of bismuthyl iodide.

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[1] *Cf.* also the communications of Gutbier and Bunz, *Zeitsch. anorg. Chem.*, **48**, 162, 294; **49**, 432; **50**, 210; **52**, 124.

Cinchonine nitrate and *potassium iodide* react with bismuth salts, even when present in very small amount, forming an orange-coloured precipitate (Léger, *Zeitsch. anal. Chem.*, **28**, 347).

8. *Potassium chromate* and *potassium dichromate* produce orange to yellow precipitates of *basic bismuth chromate*. The dichromate precipitates *bismuthyl dichromate*, $(BiO)_2Cr_2O_7$, as a yellow powder from weak acid solution. This may be distinguished from lead chromate by the fact that it is readily soluble in nitric acid, and but little soluble in cold potassium or sodium hydroxide solution.

9. *Disodium hydrogen phosphate* precipitates white crystalline phosphate, $BiPO_4$, from solutions of bismuth salts; this is *insoluble in not too concentrated nitric acid.* (Distinction from most other cations.) Alkali arsenates behave in a similar manner.

10. *Dilute sulphuric acid* does not produce a precipitate in a moderately dilute solution of bismuth nitrate. On evaporating the solution containing excess of sulphuric acid on the water bath until acid vapours no longer escape, there is left a *white saline mass which always dissolves to a clear solution* in water acidified with sulphuric acid. (Characteristic distinction from lead ion.) On standing for some time (often only after some days) a basic bismuthyl pyrosulphate, $(BiO)_2S_2O_7+3H_2O$, separates in the form of microscopic, acicular crystals, which dissolve in nitric acid.

11. On treating a solution of a bismuth salt with excess of a solution of **stannous chloride in potassium or sodium hydroxide solution** a *black precipitate* is produced, which, according to some authorities, may be regarded as bismuthous oxide, BiO, and, according to others, as a mixture of metallic bismuth with bismuth oxide:

$$Bi_2O_3+K_2SnO_2=2BiO+K_2SnO_3$$

$$\text{or}\quad Bi_2O_3+3K_2SnO_2=2Bi+3K_2SnO_3$$

This is a very characteristic and sensitive reaction.

12. *Strong reducing agents, e.g.* hypophosphorous acid, hyposulphurous acid, or formaldehyde, precipitate metallic bismuth from solutions of bismuth salts. The precipitate produced by hypophosphorous acid is re-dissolved on the addition of hydrogen peroxide.

13. The *flame* of a *Bunsen* burner is coloured bluish-green by bismuth compounds in presence of bromine compounds, and grey-blue in that of chlorine compounds. The colorations resemble those produced by copper, but are less intense.

14. When bismuth compounds are mixed with **sodium carbonate** in a hollow on charcoal, and exposed to the **blowpipe reducing flame,**

brittle granules of bismuth, which can be fractured with a hammer, are produced. Simultaneously the charcoal is coated with a slight *film of oxide*, which is orange-coloured while hot and yellow on cooling. The reduction may also be readily effected on *charcoal sticks* (p. 88). On grinding the end containing the reduced bismuth, yellow particles of metal are obtained.

15. The *deposit of metallic bismuth*, obtained as described on p. 89, is black extending into a brown film; the oxide deposit is yellowish-white (becoming black on treatment with stannous chloride and sodium hydroxide, *cf* 11. Distinction from lead oxide deposit), the iodide deposit is bluish-brown extending into a red film, and the sulphide deposit is dark brown with lighter brown film, and is not removed by ammonium sulphide (Bunsen).

16. On heating a bismuth compound, which is free from sulphur, with a mixture of equal parts of *potassium iodide* and *flowers of sulphur* (or with potassium iodide alone, if the substance already contains sufficient sulphur for the decomposition of the potassium iodide) on charcoal before the *blowpipe flame*, a very volatile scarlet deposit of *bismuth iodide* is obtained. Substances containing lead, when treated in the same way, yield a deep yellow deposit; their presence does not affect the bismuth reaction (v. Kobell). The reaction also takes place when the mixture is heated in a glass tube fused together at one end (Cornwall).

17. *Calcium carbonate*, which has been impregnated with a bismuth salt (even in very small quantity) shows a blue luminescence when brought into contact with a hydrogen flame (*cf.* Sec. 58, 21. Donau, *loc. cit.*).

18. With regard to the *microchemical detection* of bismuth ion, see Haushofer, *Mikroskopische Reaktionen*, p. 138; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., 3, 96; Schoorl, *Zeitsch. anal Chem.*, **47**, 731, 745.

SEC. 77.

(d) Cadmium, Cd, 112·40.

1. *Cadmium* is *divalent*. Metallic cadmium is like tin in colour, lustrous, ductile, and not very hard. It has a specific gravity of 8·67, melts at 321°, and boils at about 780°, but volatilises at a much lower temperature, and so can be sublimed in a glass tube. When heated on charcoal before the blowpipe it ignites and burns, producing brown fumes of oxide, which form a deposit on the charcoal. Hydrochloric acid and dilute sulphuric acid dissolve cadmium

with the evolution of hydrogen, but it is most easily dissolved by nitric acid.

2. *Cadmium oxide*, CdO, is a powder, which is sometimes light brown and sometimes dark brown; it resists the action of heat. *Cadmium hydroxide*, $Cd(OH)_2$, is white. Both compounds are readily soluble in hydrochloric, nitric, and sulphuric acids. They also dissolve in solutions of ammonium salts, especially on heating, ammonia being liberated.

3 The *cadmium salts* are colourless or white, except when the anion causes them to be coloured; some of them are soluble in water. The soluble neutral salts redden litmus in consequence of hydrolysis; the cadmium salts of volatile acids are decomposed on ignition, with the exception of the sulphate, which will stand moderate ignition.

4 **Hydrogen sulphide** and **ammonium sulphide** produce in *alkaline, neutral*, and *acid solutions bright yellow* (or under certain conditions of excess of acid and temperature orange-yellow to red) precipitates of *cadmium sulphide*, CdS. This is *readily decomposed and dissolved* by *boiling nitric, hydrochloric*, and *dilute sulphuric acids*. (Distinction from cupric sulphide). Cadmium sulphide is also insoluble in the cold in the presence of only a slight excess of hydrogen ions, so that it is *not* precipitated, at all events *completely*, from *solutions which are acid to any extent*. It is precipitated more readily from sulphuric than from hydrochloric acid solutions. The presence of much alkali chloride prevents its precipitation from even quite weak hydrochloric acid solutions. (Distinction from cupric ion. Cushman, *Zeitsch anal. Chem.*, **34**, 368) It is insoluble in alkali hydroxide, alkali sulphide, and potassium cyanide solutions. (Distinction from cupric ion.) *Ammonium thioacetate* precipitates cadmium sulphide from hydrochloric acid solution. *Sodium thiosulphate* does not give a precipitate with acid solutions of cadmium (distinction from cupric ion), but produces a slight precipitate in neutral solutions.

5 **Potassium** and **sodium hydroxide** give a white precipitate of *cadmium hydroxide*, $Cd(OH)_2$, insoluble in excess of the precipitant.

6. **Ammonia** also gives a *white precipitate of hydroxide*, which, however, *redissolves readily and completely in excess of ammonia solution* to form a colourless solution, with the formation of a complex cadmium ammonia ion, *e.g.* $Cd(BH_3)^{\cdot\cdot}{}_2$. The ammoniacal solution becomes turbid on boiling or dilution with much water, but only in the absence of ammonium salts. Potassium or sodium hydroxide precipitates cadmium hydroxide from an ammoniacal solution.

7. **Sodium carbonate** and **ammonium carbonate** produce *white precipitates of basic cadmium carbonate*, $CdCO_3+xCd(OH)_2$, which are insoluble or only very slightly soluble in excess of ammonium carbonate solution. Ammonium salts retard and influence the precipitation in the cold, but the precipitate is formed on heating, ammonia prevents the precipitation The precipitate is readily dissolved by potassium cyanide solution. It only subsides after long standing from dilute solutions, but the separation is materially promoted by heat.

8. A 17 per cent. ammoniacal solution of *ammonium perchlorate* precipitates crystalline cadmium perchlorate from an ammoniacal solution of a cadmium salt. (Distinction from cupric ion. Salvadori, *Chem. Zentr.*, 1918, I., 325.)

9. *Potassium thiocyanate* does *not* give a precipitate with solutions of cadmium salts, even after the addition of reducing agents, *e g.* sulphur dioxide. (Distinction from copper ion.)

10. On mixing cadmium compounds with **sodium carbonate** in a hollow on charcoal and heating the mixture in the **reducing flame** of the **blowpipe,** the reduced metal is immediately volatilised again and becomes oxidised on its passage through the outer flame, so that the surface of the charcoal becomes coated with a *deep yellow to reddish-brown film of cadmium oxide*, which can be most clearly seen after cooling.

In the case of very small amounts of cadmium only a very fine filmy deposit in the form of a blackish ring shading outwards into yellow to copper-red, and the interior of which shows a deep blue to violet glistening faint margin (Biewend, *Chem. Zentr.*, 1902, II., 821).

11. The *deposit of metallic cadmium*, obtained as described on p. 89, is black extending into a brown film, the oxide deposit brownish-black, extending through brown into a white film; the iodide deposit is white, and the sulphide deposit lemon-yellow, and is not removed by ammonium sulphide (Bunsen).

Analogous deposits may also be obtained by heating cadmium or cadmium compounds with reducing agents in narrow glass tubes closed at one end (Biewend, *Chem. Zentr.*, 1902, II., 821).

12. For the *microchemical detection* of cadmium ion, see Haushofer, *Mikroskopische Reaktionen*, p. 52; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 73; Schoorl, *Zeitsch anal. Chem.*, **47**, 736, 742, 748; Pozzi-Escott, *Chem. Zentr.*, 1907, II., 484.

SEC. 78.

Summary and Remarks on Group V. (Div. 2).

1. The ions of the *second division* of the fifth group may be completely separated, in the manner described, from *mercurous ion* and *silver ion*, but only incompletely from lead ion, by means of hydrochloric acid. Traces of mercuric salt, which at first are retained through adsorption by the precipitated silver chloride, are completely dissolved in the subsequent washing (G. J. Mulder).

2. (*a*) *Mercuric ion* may be distinguished from the other ions by the insolubility of its *sulphide* in dilute boiling nitric acid. This characteristic affords a convenient method of separating it from copper, lead, and bismuth ions, and from any considerable amount of cadmium ion. (Part of the cadmium sulphide, or possibly the whole of it when it is only present in traces, is retained by the mercuric sulphide. Bulow.) Care must therefore be taken to remove the *chlorides* or hydrochloric acid *completely* by washing before boiling the sulphides with nitric acid.[1] *Mercuric sulphide* dissolves readily when heated with hydrochloric acid to which a very small quantity of potassium chlorate has been added. The mercuric ion may be most easily detected in one portion of the solution by means of *stannous chloride*. *Cadmium ion* retained by the mercuric sulphide may be found by evaporating another portion of the solution to dryness in a porcelain crucible, and volatilising the mercuric chloride at a low ignition temperature in a fume cupboard. On treating the residue with a drop of hydrochloric acid and a little water, the cadmium ion is obtained in solution, and may be precipitated therefrom by means of hydrogen sulphide. (*b*) The mercuric sulphide may also be separated completely from the sulphides of lead, bismuth, and copper, but only incompletely from cadmium sulphide, by boiling the moist sulphides with sodium thiocarbonate solution (prepared as described in Sec. 59, 13, footnote. Rosenbladt, *Zeitsch. anal. Chem.*, 26, 15); or (*c*) The separation may be effected by treating the sulphides with a mixture of potassium sulphide and hydroxide solutions (Polstorff and Bulow, *Arch. d. Pharm.*, 229, 292; *Chem. Zentr.*, 1891, II., 227). Owing to the formation of complex compounds, mercuric sulphide is dissolved, and may be re-precipitated from the filtrate by means of hydrochloric acid (or, as in Polstorff and Bulow's method, by ammonium chloride), whilst the other

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[1] The completeness of the washing is shown by the final washings not giving any precipitate or turbidity with silver nitrate solution.

sulphides (in the absence of cadmium) are left free from mercury and may be dissolved in nitric acid. (*d*) The separation of mercuric ion from cupric, bismuth, and cadmium ions, and its incomplete separation from lead ion, may also be effected by heating the hydrochloric acid solution with a solution of phosphoric acid (prepared by allowing phosphorus to deliquesce in the air, and diluting the syrupy residue with water). The mercuric ion is precipitated as mercurous chloride. Lead ion may be simultaneously precipitated (v. Uslar, *Zeitsch. anal. Chem*, **34**, 391).

3. Of the other cations remaining in the nitric acid solution after separation of the mercuric ion (as in 2 (*a*)), *lead ion* may be precipitated by adding sulphuric acid. The separation is most complete when, prior to the addition of an excess of dilute sulphuric acid, the liquid has been evaporated on the water bath, until nitric acid vapours no longer escape, and then diluted with water containing sulphuric acid, and the insoluble residue of lead sulphate immediately filtered off. This residue may then be subjected to further tests by the dry method, as described in Sec. 72, 14, or it may be tested as follows: A portion of it is heated with a little potassium chromate solution, which converts the white precipitate into yellow lead chromate The latter is separated, washed, and heated with a little potassium or sodium hydroxide solution, which re-dissolves it, and, on then acidifying the clear solution with acetic acid, a yellow precipitate of lead chromate is once more obtained.

4. (*a*) After separation of the mercuric and lead ions *bismuth ion* may be separated from copper and cadmium ions by adding *ammonia solution* in excess, since the hydroxides of the two latter metals are soluble in excess of ammonia solution On dissolving the separated bismuth hydroxide in *one or two drops of hydrochloric acid* on a clock glass, and adding water, the occurrence of a *milky turbidity* confirms the presence of bismuth. (*b*) The reaction described in Sec 76, 11, depending on the formation of bismuthous oxide, is also a suitable confirmatory test.

5. The presence of any appreciable quantity of *cupric ion* may be recognised by the blue colour of the ammoniacal solution. Still smaller amounts may be detected by evaporating a portion of the solution nearly to dryness, and adding a little acetic acid and then *potassium ferrocyanide solution*.

6. (*a*) *For the separation of copper ion* from *cadmium ion*, the remainder of the ammoniacal solution is evaporated to a small volume, rendered slightly acid with hydrochloric acid, and treated

with a little *sulphur dioxide* and *potassium thiocyanate solutions*. The cuprous thiocyanate is allowed to subside in a warm place and filtered off, and the cadmium ion in the filtrate precipitated by means of hydrogen sulphide, after removal of any sulphur dioxide present. (Obviously an unnecessarily large excess of the latter must be avoided. One of the reducing agents mentioned in Sec. 75, 11 may also be used instead of sulphur dioxide.) Other methods of separating copper and cadmium ions are based upon the treatment of the sulphides with (*b*) *potassium cyanide*, or (*c*) with *boiling dilute sulphuric acid* (1 part of concentrated acid with 5 parts of water). For this purpose the solution is treated with hydrogen sulphide, and the precipitate separated from the liquid by decantation or filtration, and washed. If it is then treated as in (*b*) with a little water and a fragment of potassium cyanide, the cupric sulphate dissolves, while the yellow cadmium sulphide remains undissolved. On boiling the precipitate of the two sulphides with dilute sulphuric acid (*c*), the cupric sulphide remains insoluble, while the cadmium sulphide dissolves. On then treating the filtrate with hydrogen sulphide water, yellow cadmium sulphide is again precipitated (A. W. Hofmann). (*d*) In this last method there is a risk that some cupric sulphide may be oxidised to sulphate by the action of the air, and so be simultaneously dissolved when the precipitate is treated with sulphuric acid, with the result that a brown precipitate is again formed in the filtrate, and that this may cause a small amount of cadmium to be overlooked. Hence Cushman recommends that the sulphides should be treated with an excess of a saturated solution of sodium chloride and a little hydrochloric acid. Cadmium sulphide dissolves, and may be re-precipitated from the filtrate by means of hydrogen sulphide water. A still sharper separation is effected by treating the solution (2 c.c.) containing the copper and cadmium ions with saturated sodium chloride solution (20 c.c.) and a little hydrochloric acid, and passing a current of hydrogen sulphide into it, when the cupric ion is precipitated as sulphide. The precipitate is collected on a dry filter, and the liquid filtered into a dry test-tube. On then adding a few drops of water to the filtrate a yellow ring of cadmium sulphide separates.[1] (*e*) Kragen recommends the different behaviour of copper and cadmium ions towards pyridine as a means of detecting them in the presence of each other. Both cations are precipitated by pyridine as pyridine double salts, but the copper compound is soluble in excess of pyridine, whereas the cadmium compound is insoluble. The sulphides are dissolved in hydrochloric acid, the solution neutralised with ammonia, and an equal volume of sodium chloride solution and of pyridine added. Cadmium ion forms a white precipitate, whilst copper ion may be recognised by the deep blue colour of the solution (*Monatsh. f. Chem.*, **37**, 391; *Chem. Zentr.*, 1917, I., 531).

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[1] A method of separating cupric and cadmium ions based upon capillary analysis has been recommended by Trey (*Zeitsch. anal. Chem.*, **37**, 743).

SPECIAL REACTIONS OF THE RARER MEMBERS OF THE FIFTH GROUP.[1]

SEC. 79.

1. Palladium, Pd, 106·7.

1. *Palladium is divalent and tetravalent.* It is of rare occurrence in metallic form, sometimes alloyed with gold and silver, but especially in association with platinum or in platinum ores. The colour of palladium is somewhat darker than that of platinum, which in other respects it closely resembles. Palladium melts with very great difficulty (at 1510° to 1550°); its specific gravity is 11·4 to 11·8; it assumes a bluish tint when ignited in the air at a dull red heat, but regains its metallic lustre and light colour when more strongly ignited. It dissolves with difficulty (more readily when alloyed with other metals) in pure nitric acid, somewhat more readily when nitrous acid is present, and is hardly soluble in boiling concentrated sulphuric acid, but it is rendered soluble by fusion with potassium hydrogen sulphate, and is readily soluble in *aqua regia*. Finely divided palladium is also soluble in strong hydrochloric acid. Palladium combines with oxygen in several proportions; the most important of the oxides are palladous oxide, PdO, and palladic oxide, PdO_2. Only the salts corresponding to the former are stable, the palladic salts being readily decomposed and converted into palladous salts.

2. *Palladous oxide* is black, its hydroxide is white, and both, when strongly ignited, leave a residue of metal. *Palladic oxide* is black; when heated with dilute hydrochloric acid it dissolves, palladous chloride being formed and chlorine liberated.

3. Most of the *palladous salts* are soluble in water; they are brown or reddish-brown in colour, and their solutions are brown when concentrated and yellow when dilute; that of palladous nitrate yields a precipitate of a brown basic salt on the addition of water, if not more than a slight excess of acid is present. The palladous salts of volatile acids are decomposed on ignition, leaving a residue of palladium.

4. *Hydrogen sulphide* and *ammonium sulphide* precipitate black *palladous*

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[1] With regard to the analytical behaviour of the platinum metals, reference may be made to the comprehensive work of Mylius and Mazzucchelli, *Zeitsch. anorg Chem.*, **89**, 1 (1914); *Zeitsch. anal. Chem.*, **55**, 273; see also pp. 325–327.

sulphide from acid or neutral solutions. This precipitate is insoluble in ammonium sulphide solution, but dissolves in potassium thiocarbonate solution (distinction from lead, copper, and bismuth ions), and is *not* precipitated from the solution by *carbon dioxide*. (Distinction from mercury ion. Rosenbladt.) It dissolves in boiling hydrochloric acid, and is readily soluble in *aqua regia*.

5. *Acetylene* (as gas or in aqueous solution) produces in an *acid* solution a reddish-brown precipitate of *palladous acetylide*, which is soluble in ammonia, potassium cyanide, and sodium hydrogen sulphite solutions. This is a good method for the separation of copper, platinum, and iridium ions (Erdmann and Makowka, *Zeitsch. anal. Chem.*, **46**, 141).

6. A solution of palladous chloride yields on treatment with *potassium or sodium hydroxide* a brown basic salt, which is soluble in a large excess of the precipitant, whilst *ammonia* produces a flesh coloured precipitate of *palladous chloride ammonia*, $PdCl_2(NH_3)_2$, or $PdCl_2,Pd(NH_3)_4Cl_2$, which dissolves in excess of ammonia solution (fairly rapidly on heating, slowly in the cold) to form a colourless liquid, from which hydrochloric acid precipitates *palladosamine chloride*, $Pd(NH_3)_2Cl_2$, as a yellow crystalline precipitate.

7. *Mercuric cyanide* produces in neutral or slightly acid solutions a yellowish-white gelatinous precipitate of *palladous cyanide*, which dissolves with some difficulty in hydrochloric acid, but is readily soluble in ammonia solution. This is a particularly characteristic reaction, the sensitiveness of which, however, is influenced by the presence of other platinum metals (Mylius and Mazzucchelli, *Zeitsch. anorg. Chem.*, **89**, 15).

8. *Stannous chloride* produces, in the absence of free hydrochloric acid, a black precipitate, but in the presence of that acid it gives a red solution, changing to brown and finally to green, and becoming brownish-red on the addition of water.

9. *Sodium formate* precipitates the whole of the palladium at 50° in the form of metallic *palladium black*. Other reducing agents, such as *alcohol* in the presence of alkali hydroxide, *hydrazine sulphate* in ammoniacal or acid solution, give a precipitate of metallic palladium, which is lustrous, pulverulent, or colloidal, according to the conditions.

10. *Potassium iodide* gives a black precipitate of *palladous iodide*, which dissolves to a brown solution in excess of the precipitant. This is a particularly characteristic reaction.

11. *Potassium chloride* gives with a concentrated solution of palladous chloride a precipitate of *potassium palladous chloride*, K_2PdCl_4, in the form of golden yellow needles, which readily dissolve in water, yielding a dark brown solution, but are insoluble in absolute alcohol.

12. *Potassium nitrite* produces in solutions which are not too dilute a crystalline yellow precipitate, which becomes red on standing for some time, and is soluble in a large volume of water.

13. *Potassium thiocyanate* does not give a precipitate with solutions of palladous salts, even after the addition of sulphur dioxide. (Distinction and method of separation from copper ion.)

14. *a-nitroso-β-naphthol* produces a voluminous reddish-brown precipitate in solutions of palladous salts. This is a very sensitive reaction, which distinguishes palladium ion from the ions of the other platinum metals (W. Schmidt, *Zeitsch. anorg. Chem.*, **80**, 335).

15. *Dimethylglyoxime* gives with solutions of palladium salts a fine yellow precipitate, which is readily soluble in ammonia and potassium cyanide solutions, but is only very sparingly soluble in water, 50 per cent alcohol, and dilute acids. (Distinction from the ions of the other platinum metals, except platinum, but not from gold ion. Wunder and Thuringer, *Zeitsch. anal Chem.*, **52**, 101 and 660.) Other platinum metals also influence the sensitiveness of the reaction (Mylius and Mazzucchelli, *Zeitsch anorg. Chem*, **89**, 16).

16. *Ethylmercaptan* in 1 per cent. aqueous solution produces a *yellow coloration at once* in neutral solutions of palladous chloride, even when very dilute, but on acidification with acid, and especially after heating, a dark yellow flocculent precipitate is immediately formed (iridium, ruthenium, and osmium ions are only precipitated after heating the solution for a long time) (Claesson, *J. prakt. Chem.*, (2) **15**, 206; Mylius and Mazzucchelli, *Zeitsch. anorg. Chem.*, **89**, 16).

17. On treating *alkanet tincture* with a few drops of a solution of a palladous salt, the liquid, which is at first red, changes to orange-yellow, steel-grey, and finally green, and then on standing for some time becomes turbid and red again. If ammonia is added to the liquid while still green the colour changes to blue. Different absorption spectra correspond to these changes of colour (Formánek, *Zeitsch. anal. Chem.*, **39**, 681).

18. When ignited with *sodium carbonate* in the *upper oxidation flame*, all palladium compounds yield a grey spongy deposit of metal. On grinding this up in an agate mortar, silvery-white, malleable particles of metal are obtained.

19. Palladium compounds show the *ignition reaction*, *cf.* Sec. 85, 11.

20. On moistening partially dehydrated *borax beads* with a dilute solution of a palladous salt, and then fusing them again, *black beads* are obtained.

21. For the *microchemical detection* of palladium ion, see Haushofer, *Mikroskopische Reaktionen*, p. 107; Behrens-Kley, *Mikrochemische Analayse*, 3rd ed., p. 160; Pozzi-Escot and H. C. Couquet, *Compt. rend.*, **130**, 1073; *Chem. Zentr.*, 1900, I., 1092.

SEC. 80.

2. Rhodium, Rh, 102·9.

1. *Rhodium* is *divalent* and *trivalent*. It occurs in small quantities in platinum ores. Rhodium is an almost silvery-white, ductile metal, which is very difficult to melt (about 2000°), or, when separated by the wet method, is a grey or black powder with a specific gravity of 12·6. Compact rhodium does not dissolve in any acid, and is only soluble, even in *aqua*

regia, when it is alloyed with gold or silver, but not with platinum, copper, etc. Phosphoric acid and potassium hydrogen sulphate, when fused with rhodium, dissolve it in the form of rhodic salts When heated in chlorine it yields chlorides of variable composition (Claus, Leidié). Heated with *potassium or sodium chloride in a current of chlorine* it forms double chlorides. Sodium rhodic chloride is insoluble in alcohol. (Method of separation from platinum ion and other cations.)

2. Rhodium forms three compounds with oxygen, viz. *rhodous oxide*, RhO, *rhodic oxide*, Rh_2O_3, and the *peroxide*, RhO_2. *Rhodic oxide* is grey or black (the corresponding hydroxide being yellow or brownish-black). It is insoluble in acids, but dissolves in the same solvents as the metal (*vide supra*). Its solutions are a fine red.

3 *Hydrogen sulphide* gives, after a considerable time, especially on heating, a brown precipitate, which is either *rhodic sulphide*, Rh_2S_3, or rhodium hydrogen sulphide, $Rh(SH)_3$, according to the conditions of precipitation. This is insoluble in acids and alkali sulphide solutions, but is dissolved by bromine water or *aqua regia*

4 *Alkali monosulphides* give a brownish-black precipitate of rhodium alkali sulphide, which is insoluble in excess of the precipitant, and is decomposed by water (Leidié).

5. *Potassium hydroxide*, when added in not too large an excess to solutions of rhodium salts, immediately produces a *yellow* precipitate of the *hydroxide*, $Rh(OH)_3 + H_2O$, which is soluble at the ordinary temperature in excess of the precipitant; on *boiling* the yellow solution the *blackish-brown hydroxide*, $Rh(OH)_3$, is precipitated. (No precipitate is produced at first in a solution of rhodic chloride by means of potassium hydroxide, but on adding alcohol black hydroxide soon separates. Claus)

6 *Ammonia* produces after some time a yellow precipitate, soluble in hydrochloric acid

7 *Zinc* and also *formic acid* give a black precipitate of metallic rhodium. *Hydrazine sulphate* in alkaline (not in acid) solution, or *hydrazine hydrate* precipitates black metallic rhodium from concentrated solutions, and lustrous rhodium from dilute solutions (Gutbier and Riess, *Ber.*, **42**, 1437 and 2205). *Hydroxylamine sulphate* does not effect a reduction in acid solution (Distinction from gold ion. Jannasch and Mayer, *Ibid.*, 38, 2130.)

8 On heating a solution of rhodic chloride with *potassium nitrite* (not with sodium nitrite) it turns yellow, and an orange-yellow powder, which is only slightly soluble in water but dissolves readily in hydrochloric acid, is precipitated, whilst another portion of the rhodium is converted into a yellow salt, which is soluble in water, but precipitated by alcohol. A method of separating rhodium from ruthenium ion is based upon the insolubility of *rhodic potassium nitrite* in alcohol (Gibbs).

9. All *solid rhodium compounds* when heated in *hydrogen*, or also when ignited on platinum wire with *sodium carbonate* in the upper oxidising flame, yield the *metal*, which may be recognised by its insolubility in *aqua regia* and its solubility on fusion with potassium hydrogen sulphate. The

fused mass obtained with the latter is yellow when cold, and gives a yellow solution with water. The solution becomes red on the addition of hydrochloric acid (Bunsen).

10. Rhodium gives the ignition reaction (*cf.* Sec. 85, 14).

11. On moistening a partly dehydrated *borax bead* with a dilute solution of a rhodium salt, and fusing it, a brown bead is obtained, which appears slate-grey by reflected light.

12. The *microchemical detection* of rhodium ion is based upon the characteristics of rhodium potassium nitrite (Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 86) or of ammonium rhodium chloride (Wilm, *Ber.*, 18, 2547).

SEC. 81.

3. Ruthenium, Ru, 101·7.

1. *Ruthenium* is *di-*, *tri-*, *tetra-*, *hexa-*, and *octavalent*. It occurs in small proportion in platinum ores. The metal is brittle, greyish-white, difficult to melt (at about 1900°), and has a specific gravity of 12·26, whilst in the form of powder it is greyish-black; it is scarcely dissolved by *aqua regia*, and is not attacked when fused with potassium hydrogen sulphate.

2. It combines with oxygen to form *ruthenous oxide*, RuO, *ruthenic oxide*, Ru_2O_3 (sesquioxide), *dioxide*, RuO_2 (ruthenium oxide), and tetroxide, RuO_4 (perruthenic anhydride).[1] When the metal in powdered form is ignited in the air it forms black *sesquioxide*, insoluble in acids.[2]

3. On igniting a mixture of the metal and potassium chloride in a *current of chlorine*, the product consists of *potassium ruthenium sesquichloride*, which dissolves in water to form an orange-coloured solution. This solution yields, slowly on standing and immediately on heating, a voluminous black colloidal precipitate, which remains in suspension for a long time, and gives a pronounced coloration. This is a very sensitive reaction.

(*a*) *Potassium or sodium hydroxide*, or *ammonia*, gives a blackish-brown precipitate of sesquioxide, which is insoluble in excess of potassium or sodium hydroxide solution, but dissolves to a greenish-brown solution in excess of ammonia solution and in hydrochloric acid, forming an orange-coloured solution.

(*b*) *Hydrogen sulphide* gives a light-coloured precipitate, but only after some time; this is doubtless a mixture of black ruthenium sulphide and sulphur. The precipitate gradually becomes darker, while the liquid becomes deep blue.

(*c*) *Ammonium sulphide* gives a brownish-black precipitate, which is only sparingly soluble in excess of the precipitant.

(*d*) *Zinc* at first produces an indigo-blue coloration, owing to the reduction of the ruthenic ion to ruthenous ion; subsequently metallic ruthenium separates.

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[1] The anhydride of ruthenic acid (trioxide, RuO_3) is not known.

[2] According to Debray and Joly, the product thus obtained is in all probability a mixture of dioxide and metallic ruthenium.

(e) *Potassium thiocyanate* produces after some time (in the absence of other platinum metals) a *red* coloration, which gradually becomes *purple red*, and, on heating, a *fine violet*. This is a very characteristic reaction, which, however, is influenced by the ions of other platinum metals.

(*f*) *Potassium iodide* gives a *black* precipitate of *iodide*, gradually in the cold and immediately on heating.

(*g*) On treating the solution, which has been made slightly alkaline with sodium carbonate, with *potassium nitrite*, heating it to boiling point, allowing it to cool, and adding to it a very small quantity of colourless ammonium sulphide, the liquid becomes *crimson* and afterwards *brown* (even in the presence of the ions of other metals which occur in platinum ores). The addition of more ammonium sulphide produces a brown precipitate.

(*h*) On adding a few drops of ruthenic chloride solution to a solution of *sodium thiosulphate*, which has been treated with ammonia, an intense *purple red* coloration is produced.

4. *Ruthenium oxide* (dioxide) is a blackish-blue powder, which is insoluble in acids, but dissolves, with brown coloration, when fused with potassium hydroxide. Its *hydroxide* is dark ochre-yellow, and is soluble in acids, forming a light yellow solution. When metallic ruthenium is fused with *potassium hydroxide* and *potassium nitrate* or *chlorate* an orange-coloured mass is obtained. This contains *potassium ruthenate*, which is soluble in water, forming an orange-coloured solution. Acids or alcohol precipitate ruthenium sesquihydroxide from this solution. When chlorine is introduced into potassium ruthenate solution ruthenium tetroxide volatilises.

5. *Ruthenium tetroxide* is a yellow crystalline mass, which volatilises, even at the ordinary temperature. It melts easily and boils at a little over 100°. The golden-yellow gas has an odour recalling that of the decomposition products of nitrogen trioxide. *Ruthenium tetroxide* dissolves slowly and sparingly in water; when heated with hydrochloric acid it forms ruthenium trichloride, while chlorine is liberated. The trichloride combines with excess of chlorine to form tetrachloride. Hydroxylamine reduces the tetrachloride to trichloride. (Distinction from platinum ion.)

(*a*) *Sulphur dioxide* gives a purple-red and than a violet-blue coloration with a solution of the tetroxide.

(*b*) *Hydrogen sulphide* produces a black precipitate of oxysulphide, while the liquid assumes a transitory red colour.

(*c*) *Ruthenium tetrachloride* combines with *hydrochloric acid* to form ruthenium hydrochloric acid, H_2RuCl_6, to which the sparingly soluble potassium and ammonium salts correspond. On standing it loses chlorine and changes into the sesquichloride, which no longer gives a precipitate with ammonium chloride.

6. Solutions of ruthenium salts and the vapours from ruthenium compounds give a *black coloration with organic substances*.

7. On moistening a partly dehydrated *borax bead* with a solution of a ruthenium salt, and again fusing it, a *black bead* is obtained.

8. For the *microchemical detection* of ruthenium ion, see Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 165.

SEC. 82.

4. Osmium, Os, 190·9.

1. ***Osmium*** is *di-*, *tri-*, *tetra-*, *hexa-*, and *octavalent*. It is of rare occurrence in platinum ores as osmium-iridium. It is a black powder, or grey solid, with metallic lustre, is very difficult to melt (at about 2500°), and has a specific gravity of 22·5.

2. Both the metal and the oxides—*osmous oxide*, OsO, *osmic oxide*, Os_2O_3, and the *dioxide*, OsO_2—are oxidised when heated in the air, and yield the volatile *osmic tetroxide* (perosmic anhydride), OsO_4,[1] which may be recognised by its extremely pungent unpleasant odour, recalling that of chlorine and iodine. This is very characteristic.

3. When a little osmium is introduced on a strip of platinum foil into a gas flame about halfway up in the outer zone it renders the *flame extraordinarily luminous*. Even traces of osmium may be detected in this way in iridium, but the phenomenon is only of momentary occurrence; the test may be repeated by introducing the substance first into the reducing flame and then bringing it back again into the outer zone.

4. *Nitric acid*, especially the red fuming acid, and also *aqua regia*, dissolve osmium, forming perosmic acid. Heat promotes the solution, but also causes osmium tetroxide to volatilise. Osmium which has been very strongly ignited does not dissolve in acids. When it is fused with *potassium nitrate* and the dissolved mass *distilled* with *nitric acid* osmium tetroxide is found in the distillate. (This is a characteristic reaction of all the osmium compounds.) *Hydrogen peroxide* dissolves finely divided osmium, as obtained by reduction with zinc or magnesium, the tetroxide being formed. (Distinction from the other platinum metals. Orlow, *Chem. Zeit.*, **30**, 714.)

5. On heating osmium in *dry chlorine gas free from air*, bluish-black *osmous chloride*, $OsCl_2$, is first formed, though always in small proportion, and then the more volatile red *chloride* (tetrachloride), $OsCl_4$; if *moist chlorine gas* is used, a green mixture of the two chlorides is obtained. The dichloride dissolves to form a blue solution, the tetrachloride to form a red, and the two together a green solution, which subsequently changes to red. The solutions soon decompose with the formation of osmium tetroxide, hydrochloric acid, and a mixture of osmous oxide and osmium dioxide, which separates as a black powder.

6. On heating a mixture of osmium powder or of osmium sulphide and *potassium chloride* in *chlorine*, potassium osmium tetrachloride, K_2OsCl_6, is formed; it dissolves with difficulty in cold, but more readily in hot water

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[1] The anhydride of osmic acid, H_2OsO_4, is not known.

(*a*) *Alcohol* precipitates the salt from this solution as a red crystalline powder.

(*b*) *Potassium hydroxide* precipitates black hydroxide from the hot solution.

When potassium osmium chloride is *fused* with *sodium carbonate* greyish-black osmium dioxide, insoluble in water and hydrochloric acid, is obtained.

7. *Potassium osmic chloride* is very soluble in water. The deep red solution is readily decomposed, especially on heating, with the separation of black oxychloride. Potassium hydroxide precipitates brownish-red *osmic hydroxide* from the red solution.

8. *Osmium tetroxide* (the anhydride of perosmic acid) is white and crystalline, melts when slightly heated, and boils at about 100°. The vapours have an unbearable odour, and have a pronounced irritating action upon the nose and eyes. When heated with water it melts and slowly dissolves. The solution is colourless, has an irritating unpleasant odour, but does not show an acid reaction.

(*a*) Concentrated *potassium hydroxide solution* produces a yellow coloration in the solution.

(*b*) On distilling this alkaline solution most of the tetroxide distils (a characteristic test), whilst the remainder is decomposed into oxygen and *potassium osmate*, K_2OsO_4, and on continued boiling into osmic tetroxide, osmic hydroxide, and potassium hydroxide.

(*c*) Osmium tetroxide *decolorises indigo solution, liberates iodine from potassium iodide solution*,[1] and *oxidises alcohol* to aldehyde and acetic acid. When heated with alcohol or tannic acid in presence of hydrochloric acid a blue coloration is produced, owing to the formation of osmous chloride, $OsCl_2$.

(*d*) Potassium nitrite reduces it readily to *potassium osmate*, which separates in garnet-red crystals; the same compound is also formed when a solution of tetroxide, which has been treated with *potassium hydroxide*, and so contains perosmate ion, is reduced with *alcohol*. The *potassium osmate* may be quantitatively precipitated by means of *ammonium chloride solution*.

(*e*) *Sulphur dioxide*, added in increasing quantities to a solution of osmium tetroxide, produces successively yellow, reddish-brown, green, and finally indigo-blue colorations.

(*f*) *Ferrous sulphate* gives a black precipitate of the dioxide.

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[1] According to Orloff (*Chem. Zeit.*, **31**, 1063) this is not the case. Osmium tetroxide does not liberate iodine from a neutral solution of potassium iodide. The solution only becomes yellow, the colour changing to green on the addition of acid. A sensitive test for osmium ion has been based by E. Pinerua Alvarez (*Chem. News*, **91**, 172; *Chem. Zentr.*, 1905, I., 1483) on this reaction, which depends upon the formation of the iodine compound $OsI_2.2HI$. Two c.c. of a 1 per cent. solution of potassium iodide are treated with 20 drops of pure concentrated sulphuric acid or phosphoric acid of sp. gr. 1·7, and on then adding 1 drop of a solution of an osmium salt a green coloration, removable by shaking with ether, is obtained.

(*g*) *Stannous chloride* gives a brown precipitate, which dissolves in hydrochloric acid, forming a brown solution.

(*h*) Zinc and many metals in the presence of a free strong acid give a precipitate of metallic osmium. Sodium formate or acetylene effect a reduction to the metal.

(*i*) *Hydrogen sulphide* produces a blackish-brown coloration in an aqueous solution of osmium tetroxide, whilst on adding an acid there is formed a blackish-brown *precipitate* of *osmium tetrasulphide* or of *hydrated oxysulphide*, which is insoluble in solutions of alkali hydroxides, carbonates, or sulphides.

9. When *ignited in a current of hydrogen* all osmium compounds yield metallic osmium, whilst when ignited in the oxidising flame they yield volatile osmium tetroxide, recognisable by its odour, etc.

10. If a partly dehydrated *borax bead* is moistened with a solution of an osmium salt and again fused, a reddish-brown bead is obtained.

11. For the *microchemical detection* of osmium ion, see Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 163.

SIXTH GROUP.

Elements with Sulphides, insoluble in dilute Acids and forming Sulpho Anions.

Members of frequent occurrence: **Gold, Platinum, Tin,** (as stannous and stannic ions), **Antimony, Arsenic** (as arsenate and arsenite ions).

Members of rarer occurrence: **Iridium, Germanium, Selenium, Tellurium, Molybdenum, Tungsten.**

SEC. 83.

The members of the sixth group have (at all events in their states of higher valency) a pronounced tendency to form anions with oxygen, and thus form a transition stage in passing to the metalloids. In their states of lower valency, however, some of the more important also occur as cations, whilst in their elementary condition they show, almost without exception, the characteristics of metals. For this reason and also owing to their analytical behaviour (especially towards hydrogen sulphide) they are dealt with among the cations.

Characteristics of the Group.

Position in the Periodic System.—The members of the sixth group may be classified analytically into two groups, which is also in accordance with their position in the periodic system. On the one hand, there are the noble metals –iridium, platinum, and gold—which immediately follow one another and occupy a position in the middle of the third great period at the end of the eighth (or beginning of the ninth) horizontal series. They have but little pronounced affinity, either in the positive or negative direction, which is also shown in connection with the characteristic property of this analytical group - the tendency to form sulpho-salt anions, which in the case of these three metals is relatively slight. They all form complex compounds, in which the metals are contained in the anion.

The members of the second division of the sixth analytical group occupy positions in the fifth, sixth, and seventh groups in the periodic system On the one hand, come selenium, molybdenum, tellurium, and tungsten in succession in the vertical direction (the respective paired and unpaired members in each instance being closer to each other analytically), and, on the other hand, they form two groups of three elements following one another in the horizontal direction, viz. germanium, arsenic, and selenium, and tin, antimony, and tellurium of which again the elements occupying positions in a vertical series (the paired members of the fourth, fifth, and sixth periodic groups) closely resemble each other in their properties.

All the members of this second division occupy a position on the border-line between metals and metalloids, and their negative character is the more pronounced when that position lies towards the end of the great periods, on the one hand, or is in one of the higher periods, on the other. All form sulpho-salt anions (in accordance with the fundamental characteristic of the group). With the exception of germanium all form anions containing oxygen. Arsenic, selenium, and tellurium (and, as regards hydrogen, also antimony) occur, like the halogens, in the free condition as anions Only tin and antimony combine as cations with anions of oxygenated acids to form salts (with a tendency towards hydrolytic dissociation), whilst the other members only form salts with halogen ions

Analytical Character of the Group.– The sulphides are insoluble in dilute acids. . They combine with alkali sulphides either directly or after absorption of sulphur, to form soluble sulpho-salts, in which the members of the sixth group are present in the sulpho salt anion. Hence the ions of the above-mentioned elements, like those of the fifth group, are precipitated completely from acidified solutions by means of hydrogen sulphide. The precipitated sulphides differ from those of the fifth group, in the fact that they are soluble in solutions of the sulphides of ammonium, potassium, etc., and are re-precipitated from those solutions on the addition of acids.

To facilitate the survey we have classified the members of frequent occurrence in this group into the following divisions :—

1. Noble Metals.

Gold and Platinum (with which may be classified iridium from the rarer members). The oxides of these metals are decomposed on ignition into the metal and oxygen, and the corresponding chlorides into metal and chlorine. The precipitates produced by hydrogen sulphide, especially when formed in hot solutions, do not dissolve in boiling hydrochloric acid, and only to a slight extent, if at all, in boiling nitric acid The sulphides are less soluble in ammonium sulphide solution than those of the other members of the sixth group. On igniting the sulphides in a current of chlorine, or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, a metallic residue is left.

2. Baser Metals or Metalloids.

Antimony, Tin, Arsenic (together with the remaining rarer members). The oxides of these metals are not decomposed by ignition into the metal and oxygen, and the chlorides volatilise when heated. The sulphides are soluble in boiling hydrochloric acid (with the exception of those of arsenic), and are dissolved or decomposed by boiling nitric acid. When heated in a current of chlorine, or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate, the sulphides volatilise completely.

SPECIAL REACTIONS OF MEMBERS OF GROUP VI. OF FREQUENT OCCURRENCE.

First Division: Noble Metals.

SEC. 84.

(a) Gold, Au, 197·2.

1. *Gold* is *monovalent* and *trivalent*. Metallic gold is yellow, highly lustrous, fairly soft, and extremely ductile. When precipitated in the form of a powder, gold is brown and dull, but in the colloidal condition it is red or blue. Gold melts with difficulty at 1064°, and has a specific gravity of 19·3. It does not oxidise when

ignited in the air, and does not dissolve in hydrochloric, nitric, or sulphuric acids, but is somewhat soluble in hot concentrated sulphuric acid containing nitric acid, and readily soluble in liquids containing chlorine or liberating chlorine, as, for example, *aqua regia*. The solutions contain auric chloride. As a general rule the presence of oxidising substances (*e.g.* ferric chloride or hydrogen peroxide) or of many organic substances (alcohol, etc.) increases the solubility of gold in acids, so that it then dissolves to some extent even in hydrochloric or sulphuric acid. Liquids containing free bromine or iodine also dissolve gold. It is also soluble in potassium cyanide solution, especially in the presence of oxygen. It is not attacked on fusion with potassium hydrogen sulphate, but alkali hydroxides, in the presence of air, alkali peroxides, and alkali nitrate oxidise it at the temperature of fusion.

2. *Auric oxide* (gold oxide), Au_2O_3, is blackish-brown; the *hydroxide* is an ochre-brown or blackish-brown powder. Both compounds are reduced by light and heat, and are readily soluble in hydrochloric acid, but insoluble in dilute oxygenated acids. Concentrated nitric acid [1] and sulphuric acid dissolve hydroxide to some extent, but water re-precipitates it from these solutions. *Aurous oxide*, Au_2O, is violet-black, and is decomposed, when heated, into gold and oxygen.

3. *Oxygenated salts of gold* are practically *unknown*. *Auric chloride*, $AuCl_3$, is red to brownish-red, loses chlorine at 150° to 200°, and leaves a yellowish-white residue [2] of aurous chloride, $AuCl$, which when strongly heated is decomposed into chlorine and gold, and on treatment with water into gold and auric chloride. Auric chloride solution is brownish-red when concentrated, and reddish-yellow when dilute, and still shows a yellow colour when greatly diluted. It reddens litmus owing to hydrolysis. Auric chloride is soluble in ether, especially in the presence of hydrochloric acid, and may, therefore, be extracted from its aqueous solution by shaking with ether. (Method of separation from platinum ion and the ions of many other metals. (*Cf.* Mylius, *Zeitsch. anorg. Chem.*, 70, 203; *Zeitsch. anal. Chem.*, 51, 380.) *Auric hydrogen chloride*, $HAuCl_4$, is an acid. It crystallises in pale yellow crystals, $HAuCl_4 + 4H_2O$, which dissolve in water, forming the so-called acid gold

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[1] According to Wohlwill (Abegg's *Handbuch*, II., 1, p. 820), auric hydroxide dissolves fairly readily in nitric acid.

[2] According to F. Meyer (*Compt. rend.*, **133**, 815; *Chem. Zentr.*, 1902, I., 18), aurous chloride is grey-green.

chloride solution. Its ions are, therefore, present in all solutions of auric chloride containing excess of hydrochloric acid.

4. **Hydrogen sulphide** *precipitates the whole of the gold ion from a neutral or acid solution of auric chloride.* (*Ammonium thioacetate* effects a similar precipitation.) The brownish-black precipitate obtained in the cold is *aurous sulphide*, Au_2S_2 (L. Hoffmann and G. Krüss). From *hot* solutions hydrogen sulphide precipitates *metallic gold.* The precipitate produced by hydrogen sulphide is insoluble in hydrochloric or nitric acid, even on heating, but dissolves in *aqua regia.* The aurous sulphide precipitate is soluble both in colourless and yellow ammonium sulphide solutions, especially on heating, and still more soluble in sodium or potassium sulphide solution, sometimes leaving a residue of gold powder. When *ignited* in a current of chlorine, or with 5 parts of ammonium chloride and 1 part of ammonium nitrate, it leaves metallic gold.

5. **Ammonium sulphide** gives a brownish-black precipitate of *aurous sulphide*, Au_2S_2 which is soluble in excess of the precipitant, especially on heating.

6. **Alkali hydroxides** precipitate *auric hydroxide*, which dissolves in excess of the precipitant, with the formation of aurate ion, AuO'_2.

7. **Ammonia,** added in excess to not too dilute solutions of auric chloride, gives a yellow to brown highly explosive precipitate of "*fulminating gold chloride*" a mixture of two substances, which when dried have compositions corresponding to the formulæ $Au_2O_3.3NH_3$ (auric oxide sesquiammine), and $Cl(NH_2)Au\ NH\ Au(NH_2)Cl$ (diammino imino-diaurous chloride) Solutions containing much ammonium chloride yield only diammino-auric chloride, $(NH_2)_2AuCl$, which is not explosive. On treating these compounds with ammonia solution the halogen is eliminated In the presence of much ammonium nitrate auric tetrammine nitrate, $[Au(NH_3)_4](NO_3)_3$, is formed (E Weitz, *Liebig's Ann.*, **410**, 117).

8. **Reducing agents** precipitate *metallic gold*[1] from a solution of *auric chloride*, usually in the form of a brown powder, which, when suspended in the liquid, causes the latter to appear blue by transmitted light. Under certain conditions, the gold may also be precipitated in crystalline form or in particles reflecting a gold lustre, whilst under other conditions blue or red colloidal solutions are obtained. Of the many possible methods of precipitation by means of reducing agents the following may be mentioned: (*a*) **Ferrous salts** reduce auric chloride in its solutions, and precipitate metallic

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[1] In many cases the presence of ammonium salts has a restrictive influence

gold in the form of an extremely fine *brown powder*. The liquid in which the precipitate is suspended appears blackish-blue by transmitted light. The dried precipitate shows a metallic lustre when pressed with the blade of a knife. When the gold solution is rendered alkaline by the addition of a few drops of potassium or sodium hydroxide solution, before adding a small quantity of ferrous sulphate solution, a black precipitate is obtained instead of a dirty-green one, even when the solution is very dilute (H. Rose, Rudorff). (*b*) **Potassium nitrite** produces a precipitate of metallic gold, even in very dilute solutions, after a short time. When the liquid is excessively dilute it shows only a blue coloration at first. (*c*) *Sulphur dioxide* precipitates gold, slowly in the cold, and rapidly on heating. (*d*) On adding **oxalic acid** to a solution of auric chloride, which is free from nitric acid, and contains little, if any, hydrochloric acid or alkali chloride, and heating the liquid, carbon dioxide is evolved, and gold separates, either in golden lustrous scales or as a golden mirror-like metallic deposit on the sides of the glass vessel: $2AuCl_3 + 3C_2O_4H_2 = 2Au + 6HCl + 6CO_2$. In acid solution there is either no reduction or only an incomplete one. This, however, is the case when the gold solution is previously treated with sodium carbonate solution (Priwoznik, *Chem. Zentr.*, 1912, I, 209). (*e*) *Formaldehyde* precipitates gold in the form of lustrous crystals from strongly acid solutions (Method of separation from the ions of copper, antimony, mercury, zinc, lead, manganese, tin, and arsenic, and also from platinum which is only very slowly precipitated.) Formaldehyde precipitates gold also from alkaline solutions on heating. *Acetaldehyde* has the same effect. *Chloral hydrate* effects a reduction in alkaline, but not in acid solutions. *Dimethylglyoxime* precipitates gold completely in metallic form from boiling hydrochloric acid solutions. (*f*) *Hydrazine salts* and *hydroxylamine salts* effect complete precipitation of gold from neutral, acid, and alkaline solutions (Knoevenagel and Ebler, *Ber.*, **35**, 3055). The latter precipitant in hydrochloric acid solution, in which it does not act until the liquid has been heated to 80°, and then somewhat slowly, is the more suitable reagent when other cations which are also precipitated by hydrazine salts are present (*e.g.* platinum, iridium, and rhodium ions (Jannasch and Mayer, *Ber.*, 38, 2129 and 2130). Gold is not precipitated from its potassium cyanide solutions by hydroxylamine salts and alkali (Lainer, *Zeitsch. anal. Chem.*, 41, 305). (*g*) *Acetylene* precipitates metallic gold from acid, but not from alkaline gold solutions. (*h*) *Hydrogen peroxide* in alkaline solution, and also *sodium* and *barium peroxides*, precipitate gold, with the evolution of oxygen. (Distinction from platinum and iridium ions. Vanino and Seemann, *Ber.*, **32**, 1968). (*i*) **Stannous chloride** precipitates metallic gold as a brown powder from concentrated strongly acid solutions of auric chloride: $2AuCl_3+3SnCl_2=3SnCl_4+2Au$ **Stannous chloride containing stannic chloride** (readily prepared by mixing stannous chloride solution with a little chlorine water) produces, *even in extremely dilute slightly acid solutions*, a *purple red* precipitate, or one which is sometimes rather more *violet* or tends towards *brownish-red;* or else a similar coloration of so-called *gold purple* (*purple of Cassius*). This is a mixture of red colloidal gold with colloidal *stannic acid*[1] (Zsigmondi, *Liebig's Ann.*, **301**, 29 and 361). The precipitate is decomposed by hydrochloric acid with the separation of gold. (*k*) On treating an auric chloride solution with a few drops of *arsenic acid solution*, 2 to 3 drops of *ferric chloride solution*, and 2 to 3 drops of *hydrochloric acid*, diluting the liquid with water to 100 c.c., and adding a fragment of *zinc*, a purple coloration develops round the zinc and gradually permeates the whole liquid (Carnot, *Ber.*, **32**, 1968; *Zeitsch. anal. Chem.*, **39**, 181).

9. For the detection of small quantities of gold the following reactions, some of which are also based upon a reduction to colloidal gold, have been described: *p-Phenylenediamine* produces, even in very dilute solutions, a *green coloration* (J. E. Saul, *Chem. Zentr.*, 1913, I., 1138). *m-Phenylenediamine* produces a *yellow* to *dark brown coloration;* this is a very sensitive reaction (Siemssen, *Chem. Zeit.*, **36**, 934). *Benzidine* in *acetic acid solution* gives a *blue* to *green coloration* (Malatesta and Di Nola, *Chem. Zentr.*, 1913, II., 716). *Tetramethyldiaminodiphenylmethane* (2.5 grms. dissolved in 10 c.c. of citric acid solution, 1 : 1, and made up to 500 c.c.) gives a *purple coloration* with solutions of gold salts, or a *light blue coloration* in extremely dilute solutions (Carney, *Chem. Zentr.*, 1912, I., 854).

10. All gold compounds are reduced when heated on *charcoal sticks* (p. 88), or upon *charcoal in the blowpipe flame*. On triturating the charcoal, glistening golden particles are obtained, which are insoluble in nitric acid, but dissolve readily in *aqua regia*.

11. When borax is partly dehydrated, and the resulting mass moistened with a *dilute* solution of a gold salt and fused into a bead characteristic colorations, due to colloidal solution, are obtained.

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[1] Gold purple of similar appearance may also be produced by precipitating red colloidal gold upon white substances (paper ash, asbestos, see *Chem. Zentr.*, 1908, I., 1575). (*Zeitsch. anal. Chem.*, **41**, 303 *et seq.*)

In the presence of *gold* a ruby-red coloration is produced. After heating the bead for some time the colloidal condition disappears, the bead becoming first blue, then greenish-blue, and finally colourless If any considerable quantity of gold is present the bead, after being heated for some time, appears liver-coloured by reflected light and blue by transmitted light. In the presence of free sulphuric acid and free halogen the reaction does not take place. Platinum may mask the gold coloration (Donau, *Monatsh. f. Chem.*, **25**, 913; *Zeitsch anal. Chem.*, **44**, 205).

Analogous colorations are obtained with **alkali phosphate beads,** but large amounts of the alkali salt change the red coloration into violet. In the presence of iron the red coloration only appears after cooling

12 With regard to the *microchemical detection* of gold ion, see Haushofer, *Mikroskopische Reaktionen*, p. 50; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed, p 155, Donau, *Chem Zentr*, 1904, II., 918; Pozzi Escot, *Chem. Zentr*, 1907, I., 1160.

SEC. 85.

(b) Platinum, Pt, 195·2.

1. *Platinum* is *divalent* and *tetravalent.* Metallic platinum in the compact condition is pale steel grey, very lustrous, fairly hard, and very ductile. It melts with great difficulty at about 1750°, has a specific gravity of 21·4, and is not oxidised when ignited in the air Spongy platinum is dull grey, precipitated platinum (platinum black) is black and pulverulent. Hydrochloric acid, nitric acid,[1] and sulphuric acid[2] do not dissolve platinum, but it is soluble in *aqua regia*, especially on heating. The solution, in the presence of excess of hydrochloric acid, contains the ions of platinohydrochloric acid, H_2PtCl_6; hydrochloric acid with hydrogen peroxide also dissolves platinum. Platinum is not attacked by fusion with potassium hydrogen sulphate, but it is oxidised at ignition temperature by alkali nitrates, by alkali hydroxides in the presence of air, and by alkali peroxides Platinates, which are soluble in hydrochloric acid, are formed in the process (*cf* Leidié and Quennessen, *Chem Zentr.*, 1902, I, 907), so that platinum vessels are attacked when these substances are fused in them (*cf.*

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[1] Platinum dissolves to an appreciable extent in nitric acid in the presence of many other metals, especially when it is alloyed with silver.

[2] With regard to the action of boiling concentrated sulphuric acid, see *Zeitsch. anal. Chem.*, **52**, 576.

p. 59). A fusion mixture of ammonium sulphate and potassium or ammonium bromide also attacks platinum, whereas the individual substances do not (Méker, *Compt. rend.*, **125**, 1029; *Chem. Zentr* 1898, I, 438). Potassium cyanide solution can also dissolve platinum to some extent in the absence of air, with the evolution of hydrogen (F. Glaser, *Zeitsch. Elektrochem.*, **9**, 11)

2. *Platinic oxide*, PtO_2, is a black powder, and its *hydroxide*, $Pt(OH)_4$, a reddish-brown powder. Both are reduced on heating The hydroxide dissolves readily in dilute acids and in sodium hydroxide solutions. *Platinous oxide*, PtO, is dark violet, and its *hydroxide*, $Pt(OH)_2$, is black; both leave a residue of the metal when ignited.

3. The *platinic salts* are decomposed on ignition; they are yellow or brown in colour. *Platinic chloride*, $PtCl_4 + 5H_2O$, forms red crystals, and platinohydrochloric acid, $H_2PtCl_6 + 6H_2O$, forms brownish-red crystals. What is commonly termed platinum chloride solution is really a solution of platinohydrochloric acid, and has an acid reaction Both platinic chloride and platinohydrochloric acid are converted into *platinous chloride*, $PtCl_2$, when gently ignited, and into platinum on stronger ignition A solution of platinic chloride containing platinous chloride is dark brown in colour

4. **Hydrogen sulphide** gradually produces a brown coloration in acid or neutral solutions, and subsequently gives a black precipitate of *platinic sulphide*, PtS_2, but even after a fairly long action does *not effect a complete precipitation*[1] (The difficulty of precipitation is due to the fact that the platinum is nearly always present almost completely in the form of the complex anion, $PtCl''_6$, and only to the extent to which this is dissociated into $Pt^{\cdot\cdot\cdot}$ and $6Cl'$ is it accessible to the action of hydrogen sulphide.) On heating the solution containing the hydrogen sulphide the precipitate is immediately produced. The precipitate also readily carries down substances which by themselves are not precipitated from acid solutions by hydrogen sulphide, notably ferrous sulphide (Wilm). *Alkali sulphides*, especially polysulphides, dissolve platinic sulphide when they are used in large excess and with the aid of heat, but complete solution is slow and difficult to effect. Hot nitric acid dissolves platinic sulphide precipitated in the *cold*, forming a *dark brown solution*, but has *little action* upon the sulphide precipitated

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[1] In the presence of mercuric chloride platinum sulphide is precipitated more rapidly and completely.

from a *hot* solution. Hydrochloric acid does not dissolve platinic sulphide even on heating, but *aqua regia* dissolves it readily. When the sulphide is heated in a current of chlorine, or with a mixture of 5 parts of *ammonium chloride* and 1 part of *ammonium nitrate*, it leaves a residue of metallic platinum.

5. **Ammonium sulphide** also gives a *blackish-brown precipitate of platinic sulphide*. This dissolves slowly (more rapidly on heating) in an excess of the precipitant, especially when the latter contains ammonium polysulphide, but it is always difficult to effect complete solution. Acids precipitate it unchanged from the reddish-brown solution.

6. **Potassium chloride** or **ammonium chloride,** when added to solutions of platinohydrochloric acid which are not too dilute, produces a *yellow crystalline precipitate of potassium or ammonium platinochloride* In the case of dilute solutions the precipitates are obtained by evaporating the liquid, after addition of the precipitant, on the water bath, and treating the residue with a little water or dilute alcohol The precipitates dissolve more readily in acids than in water They are nearly insoluble in excess of potassium or ammonium chloride solution. (Potassium hydroxide or ammonia produce similar precipitates, especially in the presence of free hydrochloric acid) The precipitates are soluble in hot concentrated potassium or sodium hydroxide solution. The platinum will then be present in solution in the form of anions ($PtCl_4OH'$, $PtCl_4O''$, or PtO''_3 ?). Ammonium platinochloride leaves a residue of spongy platinum on ignition, whilst potassium platinochloride leaves platinum and potassium chloride. Complete decomposition of the latter only takes place when the ignition is carried out in a current of hydrogen, or after the addition of a little oxalic acid.

7. **Stannous chloride** produces an *intense dark red to brownish-red coloration* in solutions which contain much free hydrochloric acid, or, in the case of very minute quantities of platinum ions, a yellow coloration, but does not form a precipitate. On diluting the liquid with water, however, a precipitate is obtained. Under these conditions, there is a separation of colloidal platinum mixed with colloidal stannic hydroxide, analogous to the formation of the gold-purple of Cassius (Wöhler and Spengel, *Zeitsch. Chem. Ind. Kolloide*, 7, 213; *Chem. Zentr.*, 1910, II., 1870).[1]

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[1] The reaction with stannous chloride is only distinctive when humic substances (which may be removed by ignition) are absent, since these (including *e.g.* filter paper, which has been evaporated with *aqua regia*) show a similar coloration (Langstein and Prausnitz, *Chem. Zeit.*, **38**, 802).

8. On treating a solution of platinohydrochloric acid with **potassium iodide** in excess *a very characteristic dark red coloration*, or, in the case of very dilute solutions, a pink coloration is obtained, which may be due to the liberation of iodine, while platinic chloride ion is reduced to platinous chloride ion : $PtCl''_6+2I'=PtCl''_4+2Cl'+I_2$, as for example, $K_2PtCl_6+2KI=K_2PtCl_4+2KCl+2I$.

9. **Ferrous sulphate** does *not* give a precipitate with platinic chloride solution, unless the liquid is boiled for a very long time, in which case the chloride is eventually reduced with the separation of platinum. If, however, sodium hydroxide and then hydrochloric acid are added to the platinic chloride solution after the addition of ferrous sulphate platinum black is precipitated.

10. *Oxalic acid* and *sulphur dioxide* do *not* precipitate *platinum* from a solution of platinic chloride, even on heating, neither does *acetylene* (distinction from palladium ion), nor *hydroxylamine* in acid or alkaline (sodium hydroxide) solution, nor *hydrogen peroxide* in alkaline solution, give any precipitate. (Distinction from gold ion in each case.)

11. *Other reducing agents, e.g. formic acid* in neutral boiling solution, *glycerin and sodium hydroxide* when heated, *magnesium, zinc*, or *hydrazine* in alkaline or dilute acetic acid solution, precipitate metallic platinum as a fine black powder.

12. *Benzidine* in acetic acid solution produces a flocculent blue precipitate after a short time, even in very dilute solutions of platinum salts (Malatesta and Di Nola, *Chem. Zentr.*, 1913, II., 717)

13. On igniting a platinum compound with *sodium carbonate* on a loop of fine platinum wire in the upper oxidising flame, a spongy grey mass is obtained, which when triturated in an agate mortar yields silvery-white malleable particles of metal, which are insoluble in hydrochloric or nitric acid, but dissolve in *aqua regia*.

14. When a dilute solution of a platinum salt is absorbed by means of thin asbestos paper and the water evaporated, this process repeated several times, and the paper finally ignited and exposed to a current of gas from an unlighted Bunsen burner, *it will become incandescent*. This is a very sensitive and characteristic reaction of the platinum metals (platinum, palladium, iridium, rhodium).

15. *Borax beads* (preferably those obtained by moistening partly dehydrated borax with a dilute platinum salt solution and then fusing the mass into beads again) and *alkali phosphate beads* are coloured fawn-brown by platinum. In the presence of larger amounts of platinum the bead becomes opalescent to turbid. On longer

heating, the colour disappears, owing to the colloidal platinum uniting into a metallic film. The colour is more stable, however, than that of gold (Donau, *Zeitsch. anal. Chem.*, **44**, 205; *Chem. Zentr.*, 1908, I., 1575).

16. With regard to the *microchemical detection* of platinum, see Haushofer, *Mikroskopische Reaktionen*, p. 110; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed , p. 157; Donau, *Chem. Zentr.*, 1907, II., 1443.

SEC. 86.

Summary and Remarks on Group VI.

1. The reactions of gold and platinum ion enable these cations to be directly detected, at all events in many cases, both in the presence of many other cations and also, in particular, when only platinum and gold ion are in the solution. In the latter case advantage may be taken of the fact that gold is precipitated by many reducing agents which do not precipitate platinum (*cf.* 9 and 10 in the preceding sections). If oxalic acid is used, it is best to evaporate the solution nearly to dryness on the water bath, and if nitric acid is present, to repeat the evaporation several times after the addition of hydrochloric acid. The residue is taken up with water, and the solution, which should be nearly free from hydrochloric acid, is treated with oxalic acid, or better, with sodium oxalate, and heated for some time, so as to precipitate the gold ion completely. The filtrate from this precipitate is treated with ammonium chloride and evaporated on the water bath nearly to dryness, and the residue treated with dilute alcohol. This dissolves the excess of ammonium chloride and of oxalic acid, or of sodium oxalate and carbonate, whilst the platinum ion is left as an insoluble residue of ammonium platinochloride. If very little platinum is present, it is preferable to evaporate the filtrate from the gold to dryness and ignite the residue in order to remove the oxalic acid. The platinum is left in metallic form. It is washed and dissolved in a few drops of *aqua regia*, and further tests applied to the resulting solution.

2. A method of separating gold ion from platinum ion may also be based on the solubility of auric chloride in ether. With regard to the special application of this method, see Mylius, *Zeitsch. anorg. Chem.*, **70**, 203; *Zeitsch. anal. Chem.*, **51**, 380.

3. For the separation of gold and platinum ions from other cations, Christensen (*Zeitsch. anal. Chem.*, **54**, 158) recommends precipitation with hydrazine sulphate (in presence of barium ion,

hydrazine chloride) from a solution slightly acidified with hydrochloric acid. The precipitate will contain only gold, platinum, mercury, and a little copper.

As an appendix to this section the separation of the ions of the rest of the platinum metals from each other and from gold and platinum ions may be outlined. Mylius and Mazzucchelli (*Zeitsch. anorg. Chem.*, **89**, 1 (1914)) have studied this subject in all its details, and from their results it appears that the presence of the ions of the other platinum metals interferes to a considerable extent with the reactions of the individual ions in the pure condition, as described in Secs. 79–82. While making a general reference to the work of these chemists, we also give on p. 327 their process for the detection of the ions of platinum metals and of gold in the presence of some other cations, which nearly always accompany them. In reference to this scheme it may be pointed out that whereas the group precipitations proceed from silver ion to iron ion, the secondary precipitations (1–6) follow the reverse direction. By this means it is possible to unite the "residues" which are obtained in the first separations, and consisting mainly of iridium and ruthenium compounds, with the main portion of those metals. The analysis ends with the separation of these two ions

Mylius and Huttner (*Zeitsch. anorg. Chem.*, **95**, 257 (1916)) have studied the behaviour of platinum in a luminous gas flame, and their results indicate that the less pure the platinum the greater the deposition of soot, so that this enables an estimation of the degree of purity to be made.

SECOND DIVISION, GROUP VI: BASER METALS OR METALLOIDS

SEC. 87.

(a) Tin, Sn, 119·0.

Tin is *divalent* and *tetravalent*. Metallic tin is greyish-white, highly lustrous, soft, ductile, and crackles when bent. It can be converted into grey tin below +20°, and thereby disintegrated, and this is particularly liable to occur on exposure to great cold ("tin disease"). At about +200° it changes into rhombic brittle tin, which can readily be powdered. The specific gravity of white tin is 7·28. Tin melts at 231·8°, boils at a white heat of ignition, is oxidised when heated in the air, but only completely after long

SCHEME FOR THE DETECTION OF THE IONS OF Pd, Pt, Rh, Ru, Ir, Au, Ag, Cu, Fe.

(1 mgrm. of each in solution as chloride.)

Group Precipitation.	Secondary Separations.
I. The solution is evaporated nearly to dryness, diluted with 2 c.c. of water, and filtered from the dark precipitate. Precipitate: Silver chloride.	6. The precipitate is extracted on the filter with ammonium solution. A white precipitate indicates (on adding nitric acid to the filtrate) *Silver ion*. The dark residue on the filter is added to that in 5.
II. The filtrate from I. is saturated with powdered ammonium chloride. The precipitate is separated after one hour, and washed with a little ammonium chloride solution. Precipitate: Double chlorides of platinum, iridium, and ruthenium.	5. The ammonium chloride precipitate (to which have been added the insoluble residues obtained in 1 to 6) is heated in hydrogen finally at white heat. The metal is extracted with dilute *aqua regia*, and *platinum ion* is detected in the concentrated solution by the formation of yellow platinum ammonium chloride. The insoluble residue is ignited with 0·3 grm. of sodium nitrate in a small spoon of gold or silver. *Ruthenium* is taken up by the fused mass with yellow coloration, whilst a blue insoluble residue indicates *iridium*.
III. The filtrate from II. is evaporated to dryness with 3 c.c. of dilute nitric acid. The cold saline residue is mixed with dilute nitric acid to form a solution almost saturated with ammonium chloride, so that the easily soluble double chlorides of rhodium, gold, copper, and iron are dissolved, whilst the dark double salts of *palladium*, *iridium*, and *ruthenium* are left undissolved. This residue is washed with a very little dilute ammonium chloride solution containing nitric acid.	4. The precipitate is evaporated with hydrochloric acid, the residue dissolved in 3 c.c. of water, and the solution saturated with hydrogen sulphide. The separated flocculent sulphide is evaporated with *aqua regia*. The solution of the residue will contain *palladium ion*, which may be detected by precipitation with mercuric cyanide. Any residue containing iridium is added to that in 5.
IV. The filtrate from III. is evaporated to dryness with dilute hydrochloric acid, the residue dissolved in 5 c.c. of water with the addition of a drop of dilute hydrochloric acid, and the solution rapidly saturated with hydrogen sulphide at about 18°. The black precipitate is separated after ten minutes and washed with water. Precipitate: Sulphides of gold and copper.	3. The sulphide precipitate is dissolved in dilute *aqua regia*, and the solution evaporated. The residue is dissolved in dilute hydrochloric acid, and the solution extracted with ether. *Gold ion* may be detected by the yellow colour of the ethereal layer, and by precipitation with sulphur dioxide. The sulphide is precipitated from the aqueous layer by means of hydrogen sulphide, and the precipitate washed and ignited. The residual oxide is extracted with dilute nitric acid. *Copper ion* is indicated by the blue coloration obtained on treating the solution with ammonia in excess. Any residue insoluble in nitric acid is added to that in 5.
V. The red filtrate from IV. (6 to 8 c.c.) is treated for half an hour with hydrogen sulphide, *being meanwhile heated*. After boiling the liquid, the precipitate is separated and washed with water. Precipitate: Rhodium sulphide.	2. The sulphide precipitate is dissolved off the filter by means of hot dilute *aqua regia*, and the solution evaporated. The residue when heated with concentrated hydrochloric acid gives a pink solution, which indicates *rhodium ion*. When heated with mercaptan the solution becomes yellow. Traces of *iridium ion* may still be present in the filtrate.
VI. The filtrate from V. is boiled, oxidised with nitric acid, and treated with ammonia, and the brown precipitate of ferric hydroxide is separated. The filtrate on evaporation leaves a residue of ammonium salts, which are completely volatilised on heating.	1. The precipitate is ignited. *Ferric ion* is detected as Prussian blue in a hydrochloric acid solution of the precipitate. Any insoluble residue which may be obtained is added to that in 5.

heating, into white stannic oxide, and is attacked by chlorine and bromine, even at the ordinary temperature, with the formation of volatile chlorides or bromides. When heated on charcoal before the blowpipe it forms a white deposit on the charcoal. The cations, stannous ion, Sn$^{\cdot\cdot}$, and stannic ion, Sn$^{\cdot\cdot\cdot\cdot}$, and the anions, stannite ion, SnO''_2, and stannate ion, SnO''_3, correspond respectively to divalent and tetravalent tin (*cf.* also Sec. 88). The tendency to form cations is only very slight, Sn$^{\cdot\cdot\cdot\cdot}$ being relatively stable only in the presence of a considerable excess of acid. Hence a pronounced tendency towards hydrolysis and to the formation of *colloidal modifications*, which are often very stable, is *particularly characteristic* of tin compounds (*cf.* Sec 88, 1). Concentrated hydrochloric acid dissolves tin as stannous chloride, with the evolution of hydrogen, whilst *aqua regia*, according to the conditions, dissolves it as stannous and stannic chlorides, or only as stannic chloride. Dilute sulphuric acid dissolves it with difficulty, whilst the concentrated acid, when used in excess, converts it into stannic sulphate, with the simultaneous evolution of sulphur dioxide Very dilute cold nitric acid dissolves tin slowly, without the evolution of gas, as stannous nitrate, while ammonium nitrate is also formed. Moderately dilute nitric acid readily oxidises tin, especially on heating. The resulting white hydroxide, *metastannic acid*, $Sn(OH)_4$, is insoluble in excess of nitric acid.[1]

(*a*) **Divalent tin, Stannous ion,** Sn$^{\cdot\cdot}$, and **Stannite ion,** SnO''_2

1. *Stannous oxide* (tin monoxide), SnO, is a black or grey-black powder, which is converted into stannic oxide when heated in the air. *Stannous hydroxide* is white. When fused with potassium cyanide, stannous oxide is reduced; it is readily soluble in hydrochloric acid. Nitric acid, when used in excess, converts it into insoluble metastannic acid.

2. The *stannous salts* are colourless; those of volatile acids are decomposed on ignition, and, when access of air is allowed, leave a residue of stannic oxide. Neutral salts, soluble in water, redden litmus, owing to hydrolysis; those insoluble in water dissolve in

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[1] The products of the oxidation of tin with nitric acid vary greatly with the temperature and conditions of concentration (see Gmelin-Kraut, 7th ed., **4**, 253–254). In the presence of iron (also of aluminium or chromium) nitric acid yields a residue of tin hydroxide, which is soluble in water and doubtless contains ferric nitrate (F. H. Van Leent, *Chem. Zentr.*, 1899, I., 101). When alloyed with antimony, tin is soluble in nitric acid containing tartaric acid (Czerwek, *Zeitsch. anal. Chem.*, **45**, 507).

hydrochloric acid if they have not been ignited. Stannous salts attract oxygen eagerly from the air, and are converted partly or completely into stannic salts; hence stannous compounds are strong reducing agents. Stannous chloride also absorbs oxygen both in the crystalline condition and in solution, being converted into stannous oxychloride and stannic chloride. A solution of stannous chloride therefore soon becomes turbid, if the bottle is opened and little free acid is present, and for this reason only freshly prepared stannous chloride dissolves, forming a clear solution in water (free from air), whilst stannous chloride crystals which have been kept only form a clear solution in water containing hydrochloric acid. In the presence of tartaric acid or of ammonium chloride a turbidity is produced, owing to the formation of complex ions. Stannous chloride is soluble in ether (de Jong, *Zeitsch. anal. Chem.*, **41**, 596).

3. **Hydrogen sulphide** produces a *dark brown* precipitate of *hydrated stannous sulphide*, SnS, in *neutral* and *acid* solutions, but not, or at all events incompletely, in alkaline solutions. The presence of a very large amount of free hydrochloric acid inhibits the precipitation. This is also prevented by the presence of much oxalic acid or ammonium chloride (Clarke, see 13). *Stannous sulphide is only slightly, if at all, soluble in ammonium sulphide, but dissolves readily as ammonium sulphostannate in yellow ammonium sulphide containing polysulphides, the anion* SnS''_3 *being formed. Acids precipitate yellow stannic sulphide*, SnS_2, mixed with sulphur from this solution. Stannous sulphide is soluble in potassium or sodium hydroxide solution, complete solution being promoted by heat. Sodium peroxide solution dissolves stannous sulphide as sodium stannate. Hot hydrochloric acid dissolves it with the evolution of hydrogen sulphide; boiling nitric acid converts it into insoluble metastannic acid. On *igniting* stannous sulphide in a **current of chlorine,** or with a mixture of 5 parts of **ammonium chloride** and 1 part if **ammonium nitrate,**[1] or in a current of *bromine vapour* containing carbon dioxide (Jannasch and Rose, *Zeitsch. anorg. Chem.*, **9**, 194), it volatilises completely, being meanwhile decomposed.

4. *Ammonium thioacetate* precipitates stannous sulphide from a solution of stannous ion containing hydrochloric acid. On heating the liquid the precipitation is complete.

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[1] If the latter operation is carried out in a glass tube fused together at the bottom, or in a current of air, the tin will be found in the sublimate as stannic chloride.

5. *Sodium thiosulphate* does not at first produce a precipitate in *acid* solutions of stannous salts, but sulphur dioxide is liberated to some extent. Not until after some time is a white precipitate formed ; this precipitate, consisting of a mixture of stannic sulphide and stannic hydroxide, rapidly subsides. If the stannous solution was very acid, the precipitation is only complete when the liquid is suitably diluted and a large excess of thiosulphate added. *Sulphur dioxide* is reduced by stannous chloride, stannic chloride and hydrogen sulphide being formed : $3SnCl_2+6HCl+SO_2=3SnCl_4+2H_2O+H_2S$. Since the hydrogen sulphide acts both on the solution of the tin salt and upon the sulphur dioxide, stannic sulphide or stannous sulphide and sulphur may be precipitated according to the conditions (Donath, *Zeitsch. anal. Chem.*, 36, 663). These reactions may also take place in a slightly acid solution through the action of sodium thiosulphate.

6. **Ammonium sulphide** also produces a precipitate of hydrated stannous sulphide.

7. **Potassium** or **sodium hydroxide, ammonia,** and also **ammonium carbonate,** give a *voluminous white precipitate of stannous hydroxide*, $Sn(OH)_2$, *which dissolves readily in excess of potassium or sodium hydroxide solution, with the formation of alkali stannite*, $Sn(OK)_2$, but is insoluble or, at most, only very slightly soluble in excess of the other precipitants. When the alkaline solution is rapidly evaporated, alkali stannate, $SnO(OK)_2$, remains permanently in solution, whilst metallic tin is precipitated ; if, on the other hand, the solution is slowly evaporated, anhydrous black stannous oxide separates, and this may also be precipitated merely by leaving the alkaline solution exposed to the air. *Tartaric acid* prevents the precipitation by alkali hydroxides or carbonates.

8. On adding a few drops of a solution of **bismuth nitrate** to a solution of alkali stannite (obtained as described in 7 by the addition of excess of alkali hydroxide to a stannous chloride solution), a white precipitate, *rapidly turning black*, is obtained (*cf.* Sec. 76, 11). The reaction is very sensitive. It depends upon the reduction of the bismuth hydroxide first precipitated, and the conversion of the stannite ion into stannate ion, $SnO''_2+O=SnO''_3$.

9. **Auric chloride** produces a brown, reddish-brown, or even a purple precipitate (*cf.* Sec. 84, 8 (i)) in solutions of stannous chloride or of a stannous salt to which hydrochloric acid has been added, according to whether the solution contains more or less stannic chloride or is more or less concentrated.

10. If stannous chloride or a solution of a stannous salt mixed with hydrochloric acid is added to excess of **mercuric chloride** solution, a white precipitate of mercurous chloride is obtained: $2HgCl_2+SnCl_2=Hg_2Cl_2+SnCl_4$ (*cf.* Sec. 74, 6).

11. If a liquid containing a *stannous salt* and hydrochloric acid is treated with a mixture of **potassium ferricyanide** and **ferric chloride** solutions, a precipitate of Prussian blue is immediately obtained, owing to the reduction of the ferric ferricyanide, $Fe[Fe(CN)_6]$ to ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$:

$$4Fe[Fe(CN)_6]+4HCl+2SnCl_2=Fe_4[Fe(CN)_6]_3+H_4[Fe(CN)_6]+2SnCl_4$$

This reaction is extremely sensitive, but is only decisive in the absence of other reducing substances.[1]

12. A solution of *ammonium molybdate* containing sulphuric acid is reduced by stannous compounds, with the production of a *blue coloration.* The reaction is sensitive, but only decisive in the absence of other reducing agents.

13. **Oxalic acid** produces in neutral or slightly acid solution a granular white precipitate of stannous oxalate, SnC_2O_4, which rapidly subsides (Distinction from stannic salts.) Concentrated solutions yield a precipitate immediately, dilute ones only after some time.

Ammonium chloride prevents the precipitation. A solution of a stannous salt, which has been treated with ammonium chloride and a large amount of oxalic acid does not give a precipitate with hydrogen sulphide.

14. *Hydrogen peroxide* precipitates the whole of the stannous ion as white, flocculent *stannic hydroxide* from a hot solution of a stannous salt, which has been neutralised with the smallest possible amount of alkali hydroxide (W. French).

15. **Zinc** precipitates *metallic tin* from *solutions of stannous salts,* which have been treated with *not too much hydrochloric acid;* the precipitate is in the form of grey flakes or a spongy mass; if the test is carried out in a platinum basin, the platinum will *not* be stained *black.* (Distinction from antimony ion.) The separated tin dissolves in hydrochloric acid after removal of the zinc.

16. On heating a hydrochloric acid solution of a *stannous salt* with a little *ammonium carbide,* a characteristic odour of methyl-tin

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[1] Ferric chloride and potassium nitrate may be used in an analogous manner for the detection of stannous compounds (Blum, *Zeitsch. anal. Chem.*, **44**, **11**). In that case a brown coloration is produced (*cf.* Sec. 61, 12).

trichloride will be produced at the moment of boiling (Hilpert and Ditmar, *Ber.*, **46**, 3738).

17. If stannous compounds are mixed with *sodium carbonate* and a little *borax*, or better, with a mixture of equal parts of *sodium carbonate* and *potassium cyanide*, or with *sodium formate*, and exposed in a hollow on charcoal to the **inner blowpipe flame,** a malleable granule of metallic tin will be obtained. The best way of recognising this is to grind up the charcoal vigorously with a little water in a mortar and to wash away the particles of charcoal. For further identification, the metallic tin may be dissolved in hot hydrochloric acid, and confirmatory tests applied to the solution. If the tin is more strongly heated, a white deposit of oxide will be formed on the charcoal. Since the reduction before the blowpipe is only successful with a good reducing flame, it is frequently preferable to *fuse* the substance with *sodium carbonate* and potassium cyanide in a *porcelain crucible*. The reduction may also be readily effected on a charcoal stick (p. 88).

18. On adding a trace of a tin compound to a **borax bead** *coloured faintly blue* with *cupric oxide*, and then heating the bead in the **lower reducing area** of a non-luminous gas flame (p. 82), it will become reddish-brown to ruby-red, owing to the reduction of the divalent copper into the monovalent condition (*cf.* Sec. 75, 22). This reaction does not take place without the intervention of a tin compound. The presence of iron interferes with the reaction, since it produces a red coloration even in the absence of tin (Lutz, *Zeitsch. anal. Chem.*, **47**, 17). The blowpipe flame cannot replace the gas flame in the test, nor can the upper reducing area of the latter flame be used, since in either case the divalent copper may be reduced to the monovalent condition without the action of tin.

19. With regard to the *microchemical detection* of divalent tin, see Haushofer, *Mikroskopische Reaktionen*, p. 153; Behrens Kley, *Mikrochemische Analyse*, 3rd ed., p. 100; Streng, *Ber.*, **22**, Ref. 31 See also Sec. 88, 19.

SEC. 88.

(β) Tetravalent Tin, Stannic ion, $Sn^{\cdot\cdot\cdot\cdot}$, and Stannate ion, SnO''_3

1. *Stannic oxide*, SnO_2, is a white to straw-yellow powder, which, on heating, becomes transitorily brown. When heated with concentrated sulphuric acid or fused with potassium hydrogen sulphate it yields compounds from which water precipitates the whole of the stannic ion. Other acids do not attack stannic oxide; when the

oxide is heated with ammonium chloride, the tin volatilises as stannic chloride.

Tetravalent tin forms a series of hydroxides (all white) of different molecular weight and varying in their degree of hydration, according to the amount of water in their environment. Those of most frequent occurrence are *stannic hydroxide*, *stannic acid* (orthostannic acid, α-stannic acid), and *metastannic acid* (β-stannic acid), whilst *parastannic acid* (γ-stannic acid) is also known. According to Engel (*Compt rend.*, **124**, 765, and **125**, 161, 651, 709), these compounds have the following formulæ: Air-dried stannic acid, H_2SnO_3,H_2O; metastannic acid, $H_2Sn_5O_{11},9H_2O$; parastannic acid, $H_2Sn_5O_{11},7H_2O$ After drying *in vacuo* these compounds have the following formulæ respectively: H_2SnO_3, $H_2Sn_5O_{11},4H_2O$, and $H_2Sn_5O_{11},2H_2O$. All three have both acid and slightly basic characteristics. Stannic hydroxide (stannic acid), precipitated by alkali hydroxide from stannic chloride solution, is readily soluble in hydrochloric acid The hydroxide (metastannic acid), obtained by the action of nitric acid on metallic tin, does not dissolve in hydrochloric acid When boiled with hydrochloric acid, however, it is converted into metastannic chloride (according to Engel, an oxychloride, $Sn_5O_9Cl_2,4H_2O$, and therefore perhaps more appropriately termed stannyl chloride– Treadwell), which is sparingly soluble in hydrochloric acid, and after decantation of the excess of acid, dissolves in water to form a solution, which is usually opalescent [1] The phenomena described above have, to a large extent, been explained by the colloidal investigations of recent years. For example, W. Mecklenburg [2] has shown that the varying size of the particles is a fundamental cause of the differences between the various stannic acids, and that upon this depends essentially the capacity of stannic acid gel to redissolve ("peptisation" capacity). Zsigmondy [3] and his pupils have found that a second cause is the difference in the distances by which the particles are separated. A complete theory of the facts, however, in this complicated branch of science has not yet been formed, and as Zsigmondy points out, this can only be done by a simultaneous consideration of both chemical and colloido-chemical processes. For further particulars reference may be made to the literature on colloidal chemistry, and in particular to Zsigmondy's comprehensive text-book already mentioned.

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[1] In accordance with the fact that it may be regarded as a compound of stannic oxide with stannic acid ($4SnO_2+H_2SnO_3$), metastannic acid may be converted by the energetic action of alkali and also by that of hydrochloric acid into orthostannic acid. Conversely, orthostannic acid compounds in dilute solution are converted more or less completely into metastannic acid compounds, in consequence of hydrolysis.

[2] *Zeitsch. anorg. Chem.*, **74**, 207.

[3] Zsigmondy, *Kolloidchemie*, 2nd ed., Leipzig, 1918, p. 127 *et seq.*, and pp. 238–263. Further references are given there.

2. The *stannic salts* are colourless. Solutions of the neutral salts redden litmus in consequence of hydrolysis Since tetravalent tin has only weak basic properties, the hydrolysis proceeds so far that the salts are decomposed by water, with the separation of stannic hydroxide (or basic salts). The chemical behaviour of stannic salts depends entirely upon their previous treatment, and accordingly two series of salts, α- and β-, or ortho- and metastannic acid salts, corresponding to the two main types of stannic acid, are known. In the case of stannic chloride hydrolytic dissociation in the cold only takes place when the solution is very dilute. The salts corresponding to volatile acids are decomposed on ignition and leave stannic oxide. Anhydrous stannic chloride, $SnCl_4$, is a volatile liquid which fumes strongly in the air. It dissolves in cold water to form a solution of stannic chloride. This does not give a precipitate either with concentrated hydrochloric acid or (unless it is very dilute) with sulphuric acid, and does not become yellow on the addition of stannous chloride, whereas metastannic chloride is precipitated by concentrated hydrochloric acid and by sulphuric acid, and its solution gives a yellow coloration with stannous chloride. Dilute solutions of either chloride are decomposed on boiling, that of metastannic chloride with especial rapidity.

3. On *fusing* stannic oxides, stannic acid, or metastannic acid with *alkali hydroxides*, *alkali stannates*, soluble in water, are produced; acids, even carbon dioxide, precipitate stannic hydroxide (stannic acid) from the solutions of these salts. When fused with alkali carbonates only a portion of the stannic oxide is converted into alkali stannate.

4. **Hydrogen sulphide** in excess produces in concentrated solutions of stannic chloride containing a moderate quantity of free hydrochloric acid, a permanently *pale yellow* precipitate of stannic sulphide, SnS_2, containing stannic hydroxide. In the case of dilute solutions or of those containing less acid, the precipitate is not always immediately formed, and only gradually becomes intense yellow. Very dilute solutions not containing free acid yield after some time a precipitate, which is white at first and subsequently yellow. Heat promotes the precipitation.

Alkaline solutions do *not* give a precipitate, and the presence of a *very large amount of free hydrochloric acid* also prevents the precipitation. In the presence of other metals which are precipitable by hydrogen sulphide, precipitates which are frequently of a *characteristic* brownish colour, probably sulphostannates, are produced in solutions of stannic salts. Hydrogen sulphide does not precipitate tin from many solutions containing the tin in complex ions. For example, *oxalic acid*, when added in sufficient quantity (35 to 10 parts of oxalic acid to 1 part of tin), prevents the precipitation. (Distinction from antimony and arsenic ions. Clarke, Lesser.) Hydrofluoric acid also inhibits the precipitation of stannic sulphide (but not that of stannous sulphide) (Franz Fischer and Thiele, *Zeitsch. anorg. Chem.*, **67**, 302). (Distinction from antimony when present in the trivalent condition. Le Roy W. McCay, Thiele, *Zeitsch. anal. Chem.*, **51**, 680, 682.) In like manner the addition of a large amount of *phosphoric acid* (an equal volume of a solution of sp. gr. 1·3) prevents the precipitation of tetravalent, but *not* that of *divalent* tin ion. (Distinction from antimony ion. Vortmann and Metzl, *Zeitsch. anal. Chem.*, **44**, 532.) *The precipitates produced by hydrogen sulphide* dissolve somewhat sparingly in ammonia solution, are nearly insoluble in cold or slightly heated ammonium carbonate solution, and insoluble in potassium bisulphite solution, but dissolve *readily* in potassium or sodium hydroxide solution,[1] in sodium peroxide solution, and solutions of *alkali sulphide* (incompletely in ammonium monosulphide, completely in ammonium polysulphide solution), in *boiling concentrated hydrochloric* acid, in oxalic acid solution, and in *aqua regia*.

The precipitate produced by hydrogen sulphide in metastannic chloride solutions (stannic sulphide containing metastannic acid) is slowly formed, especially in dilute solutions; it becomes more or less brown when allowed to remain below the liquid. Sodium hydroxide solution in excess dissolves stannic sulphide from it, leaving an insoluble residue of sodium metastannate (Barfoed). *Concentrated nitric* acid converts all the precipitates produced by hydrogen sulphide into *metastannic acid*. When heated in a *current of chlorine* or of *carbon dioxide charged with bromine* the precipitates behave like stannous sulphide (Sec. 87, 3), as is also the case when they are ignited with a mixture of 5 parts of *ammonium chloride* and 1 part of *ammonium nitrate*. On fusing the precipitates produced by hydrogen sulphide with *sodium nitrate and carbonate*, *sodium sulphate*, *stannic oxide*, and a little *sodium stannate* are obtained. If a solution of the precipitates in potassium or sodium hydroxide solution is boiled with the *oxides of bismuth or copper* the sulphides of these metals are formed, whilst alkali stannate remains in solution.

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[1] Lime-water in excess converts stannic sulphide into an insoluble white compound (probably stannic hydroxide). Distinction from antimony and arsenic ions, the sulphides of which are soluble in lime-water (Dancer, R. Marburg, *Zeitsch. anal. Chem.*, **39**, 47).

5. *Ammonium thioacetate* precipitates *stannic sulphide* from hydrochloric acid solution; the precipitation is complete on heating the liquid.

6. *Sodium thiosulphate* produces a white precipitate of *stannic sulphide* containing stannic hydroxide in an acid solution of stannic chloride.

7. **Ammonium sulphide** *precipitates yellow hydrated stannic sulphide, which dissolves readily in excess of the precipitant. Acids re-precipitate the stannic sulphide unchanged from this solution.*

8. **Potassium** or **sodium hydroxide** produces *white* precipitates of *stannic hydroxides, readily soluble in excess of the precipitant, in stannic chloride solutions.* Potassium hydroxide precipitates from metastannic chloride, metastannic acid, which is soluble in a moderate excess of the precipitant. If a larger excess is added, potassium metastannate separates; this is only sparingly soluble in potassium hydroxide solution, but is re-dissolved by water. Sodium hydroxide produces in metastannic chloride solution a white precipitate of sodium metastannate, which does not dissolve in excess of sodium hydroxide solution. Tartaric acid prevents the precipitation by alkali hydroxide from stannic chloride solution, but not from metastannic chloride solution.

9. **Ammonia** behaves like potassium or sodium hydroxide, except that the precipitate does *not* dissolve in excess of the precipitant, even in the case of solutions of α-stannic compounds.

10. **Potassium carbonate** produces a white precipitate in solutions containing α-stannic salts. The precipitate of *stannic hydroxide* containing potassium hydroxide dissolves in excess of the precipitant, but separates again on standing. The precipitate produced by sodium carbonate is insoluble or, at most, very sparingly soluble in excess of the precipitant.

The white precipitates produced by alkali carbonates in solutions of metastannic chloride do not dissolve, or do so only to a slight extent in excess of the precipitant.

11. **Sodium sulphate** or **ammonium nitrate** (as indeed most neutral alkali salts) precipitate *the whole of the stannic ion* as *ortho-* or *metastannic acid* from solutions of *α- and β-stannic salts*, provided that they are not too acid. Heat promotes the precipitation. In this case it is a question of the separation of the stannic acid present (which has been dissociated in consequence of hydrolysis), first in colloidal solution (hydrosol), and then in the form of an amorphous precipitate (hydrogel), owing to the flocculating action of neutral salts (electrolytes) dissociated into ions (*cf.* pp. 35 and 11).

12 Metallic **zinc** added to stannic chloride solution containing free hydrochloric acid precipitates metallic tin in the form of grey flakes or as a spongy mass. If the test is made in a platinum basin, the latter is *not* stained *black*. (Distinction from antimony) After removal of the zinc, the precipitated tin re-dissolves in hydrochloric acid (Distinction from antimony.)

13 Metallic **iron** reduces stannic chloride to stannous chloride, but does not precipitate tin (Distinction from antimony ion.) Metallic *copper* has the same effect after long-continued boiling as iron in the cold The resulting solution precipitates mercurous chloride from a solution of mercuric chloride (Pattinson Muir).

14 Stannic compounds are not reduced by *hydroxylamine* or *hydrazine*.

15. When stannic compounds are evaporated to dryness with *urea* and excess of *sodium hydroxide solution* and the residue heated, a black spot is left. (Distinction from stannous compounds)[1]

16 When heated with *aluminium carbide*, hydrochloric acid solutions of tetravalent tin, like those of divalent tin, yield *methyl tin trichloride*, which has a characteristic odour (*cf.* Sec 87, 16).

17 When heated before the **blowpipe** or in the **gas** flame the compounds of tetravalent tin behave in the same way as those of divalent tin (*cf.* Sec. 87, 17 and 18). Stannic oxide is also readily reduced when fused with *potassium cyanide* in a glass tube or crucible.

18 If a glass rod, or better, a narrow test-tube is dipped into a solution of stannic chloride containing free hydrochloric acid, and then heated in a Bunsen gas flame, a pale blue coloration will be imparted to the part of the flame in immediate contact with the glass (Schmatolla, *Chem. Zeit.*, **25**, 468).

19 For the *microchemical detection* of tetravalent tin, see Haushofer, *Mikroskopische Reaktionen*, p. 156; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed , p. 99; Streng, *Ber* **22**, Ref. **34**:

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[1] Reichard, *Pharm. Zentralhalle*, **47**, 391.

Schoorl, *Zeitsch. anal. Chem.*, **47**, 379, 381 ; *cf.* also Gmelin-Kraut-Friedheim-Peters, *Handb. anorg. Chem.*, IV., **1**, 258, 975, 1003; Denigès, *Zeitsch. anal. Chem.*, **38**, 309.

SEC. 89.

(b) **Arsenic,** As, 74·96.

Arsenic is *trivalent* and *pentavalent*. Elementary arsenic is *black* in the microcrystalline condition (J. W. Retgers), but in the distinctly crystalline condition it is *steel-grey* and highly lustrous. It retains its lustre in dry air, but loses it in moist air, becoming superficially oxidised ; hence commercial arsenic appears dull, with a bronze-coloured shimmer on the facets of its crystals. Arsenic is not very hard, is very brittle, and volatilises above 360° under ordinary pressure without previously melting. It melts at about 817°. The yellow vapours first formed in the air on volatilisation have an extremely characteristic *garlic-like odour*, which is due to the resulting *yellow* modification of arsenic, which is unstable in the light. *These vapours are poisonous.* If arsenic is heated with free access of air it burns—with a bluish flame if strongly heated—producing a white smoke of arsenic trioxide, which forms a deposit on a cold surface. If it is heated in a tube closed at the bottom it volatilises for the most part unoxidised, whilst if heated in a current of carbon dioxide it volatilises completely without oxidation, and is deposited as a sublimate (*arsenic mirror*) above or beyond the heated place. This sublimate is usually grey and lustrous (crystalline) at the heated place, whilst further on it is black (microcrystalline). When it is heated in a current of hydrogen, a more volatile yellowish-brown sublimate is also formed in addition to the arsenic mirror (according to Retgers, solid hydrogen arsenide). According to Reckleben Scheiber, and Strauss (*Zeitsch. anorg. Chem.*, **70,** 255), the yellow par of the mirror is also elementary arsenic. Arsenic is slowly oxidise to trioxide when in contact with air and water. Hot dilute nitri acid partially oxidises it to trioxide, which is only slightly solubl in excess of acid, whilst strong nitric acid partially converts it int arsenic acid. It is not dissolved by hydrochloric acid or dilut sulphuric acid. Boiling concentrated sulphuric acid oxidises it t arsenic trioxide, with the evolution of sulphur dioxide. It is readil of luble in *aqua regia* as arsenic acid

ext

(α) Trivalent Arsenic.

Trivalent arsenic occurs both as *cation* (arsenious ion), $As^{\cdots}$, and also as anion (arsenite ion), AsO'''_3.

1. *Arsenic trioxide*, As_2O_3, or As_4O_6 (arsenious anhydride, frequently also termed *arsenious acid* in accordance with the older nomenclature; white arsenic), is *very poisonous*. In the amorphous condition it is a colourless, transparent glass-like mass, and in the crystalline condition it is a white mass, resembling porcelain, or occurs in well formed crystals. When ground up it has the appearance of a heavy, sandy, white powder. *It volatilises, when heated, in white odourless vapours.* If the heating is effected in a glass tube a sublimate consisting of octahedra and tetrahedra is obtained. The trioxide resembles a fatty substance in being moistened only with difficulty by water. It is only slightly soluble in cold water (the crystalline form in 80 and the vitreous form in 25 parts), but dissolves more easily in hot water. The solution shows only a slight acid reaction. It is dissolved in considerable quantity as arsenite ion by potassium and sodium hydroxide solutions. Hydrochloric acid also dissolves it to a considerable extent. It is dissolved as arsenic acid by boiling *aqua regia*. Arsenic trioxide is frequently used as a reducing agent. Hydrogen in the nascent condition reduces it to elementary arsenic (see also 12). *If a granule of arsenic trioxide* (*a*) *is placed in the point of a drawn-out glass tube* (Fig. 42), and above it a **fragment of charcoal** (*b*) obtained by cutting freshly-ignited *wood charcoal*, and first the charcoal and then the arsenic trioxide are heated to ignition temperature, the vapours of the arsenic trioxide will be reduced by the glowing charcoal and a *mirror of elementary arsenic* formed at (*c*); and this volatilises and emits the garlic-like odour, when the tube is cut off between *c* and *b*, and heated in an inclined position, so that *c* is uppermost. This is the most simple and trustworthy method of identifying pure arsenic trioxide.

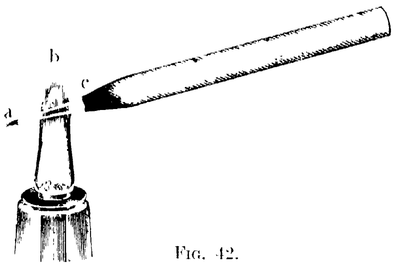

FIG. 42.

2. The *arsenites* (salts of arsenious acid) are decomposed for the most part on ignition, being converted either into arsenic, which

volatilises, and arsenate (salt of arsenic acid), or into arsenic trioxide and metallic oxide. Of the arsenites, only those of the alkali metals are soluble in water[1]: those which are insoluble in water are dissolved, or at all events decomposed, by hydrochloric acid. Anhydrous *arsenic trichloride*, $AsCl_3$, is a colourless volatile liquid, which fumes in the air, and is miscible with a small amount of water. On the addition of more water it is decomposed into arsenic trioxide, part of which separates, and hydrochloric acid, whilst the remainder of the arsenic remains in solution as arsenite ion. *On heating and evaporating a solution of arsenic trioxide in hydrochloric acid, arsenic trichloride volatilises with the hydrogen chloride.* When such a solution is heated in a distillation apparatus, the arsenic is obtained in the distillate containing hydrochloric acid. *By repeated distillation of the solution with the addition of fresh quantities of hydrochloric acid, the arsenic may be quantitatively distilled.*

3. **Hydrogen sulphide** *produces immediately in acid solutions of trivalent arsenic a bright yellow precipitate of arsenic trisulphide* (arsenic sulphide), As_2S_3. The complete precipitation is not prevented even by a large excess of *concentrated hydrochloric acid.* An aqueous solution of arsenic trioxide gives only a yellow coloration with hydrogen sulphide, owing to the formation of colloidal arsenic trisulphide, without forming a precipitate, and aqueous solutions of the neutral alkali arsenites also yield no precipitate. If, however, a strong acid is added, a bright yellow precipitate is at once obtained[2] *No precipitate is produced in alkaline solutions.*

The precipitate of arsenic trisulphide is rapidly and completely dissolved by solutions of alkali hydroxides, alkali carbonates, and alkali sulphides. Freshly precipitated arsenic trisulphide is also soluble in alkali hydrogen sulphites ($NaHSO_3$) *Arsenic trisulphide* is practically insoluble in hydrochloric acid, even when boiling and concentrated.[3] It is readily decomposed and dissolved by boiling nitric acid.

On fusing arsenic trisulphide with sodium carbonate and sodium

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[1] The solutions are partially oxidised on standing, with the formation of arsenate ion (Friedheim and Michaelis, *Zeitsch. anal. Chem.*, **34**, 541).

[2] Certain colloids (*e.g.* gum arabic) prevent this flocculation of arsenic trisulphide (Lefort and Thibault, *Zeitsch. anal. Chem.*, **22**, 237). On the other hand, we can only confirm the statement of Spiller (*J. prakt. Chem.*, **73**, 39) that citric acid prevents the precipitation by hydrogen sulphide, even in the presence of another free acid, in so far as it applies to very dilute solutions.

[3] After long continued boiling in an open vessel a considerable amount of arsenic trisulphide dissolves in dilute hydrochloric acid, or even in water, with the evolution of hydrogen sulphide.

nitrate, sodium arsenate and *sodium sulphate* are obtained. On heating it in a current of chlorine or with a mixture of 5 parts of ammonium chloride and 1 part of ammonium nitrate in a glass tube through which passes a current of air, it is completely volatilised. The arsenic will be found as arsenic trichloride in the sublimate. When a solution of arsenic trisulphide in ammonia solution is heated with hydrogen peroxide in excess, a clear solution containing arsenate ion and sulphate ion is obtained On boiling a solution of arsenic trisulphide in sodium sulphide solution, or in potassium or sodium hydroxide solution, with *bismuth hydroxide, carbonate, or nitrate,* bismuth sulphide and arsenite ion are formed. On boiling such a solution with cupric oxide, cuprous sulphide and arsenate ion are formed.

4 **Ammonium sulphide** *also effects the formation of arsenic trisulphide* This is not precipitated, however, when the solution is neutral or alkaline, but remains in solution as *sulphoarsenite ion.* On adding free acid to the solution it is immediately precipitated. If the ammonium sulphide contains polysulphide, sulphur separates with the arsenic sulphide on the addition of hydrochloric acid, and under certain conditions this may prevent the presence of small amounts of arsenic trisulphide from being recognised In such cases the sulphur may be extracted and the arsenic sulphide detected by shaking the liquid with benzene or petroleum spirit (R Fresenius, *Zeitsch anal Chem*, **33,** 573), or with carbon bisulphide (Musset, *Pharm Zentralhalle*, **34,** 737)

5. **Ammonium thioacetate** produces a white turbidity in hydrochloric acid solutions of arsenites in the cold, whilst on heating it causes an immediate and complete precipitation of *arsenic trisulphide* (R Schiff and N. Tarugi, *Ber*, **27,** 3137).

Sodium thiosulphate precipitates arsenic trisulphide readily and completely from an acid solution.

6. **Silver nitrate,** added in slight excess to an aqueous solution of arsenic trioxide, produces no precipitate, or at most a yellowish-white turbidity, but on adding a little *ammonia solution* a *yellow precipitate of silver arsenite*, Ag_3AsO_3, will be obtained. In the case of solutions of neutral alkali arsenites, an almost white precipitate, only becoming yellow on the addition of a little alkali hydroxide, is obtained. *Silver arsenite is readily soluble in nitric acid*, and also (in the presence of a little alkali nitrate) in ammonia solution (with the formation of the silver-ammonia complex, $Ag(NH_3)^{\cdot}_2$). It is also not insoluble in ammonium nitrate solution. Hence, if a small

amount of the precipitate is dissolved in much nitric acid, and the solution neutralised with ammonia, the precipitate does not re-appear, since it remains dissolved in the resulting ammonium nitrate solution. The most sensitive method of applying the reaction is to pour a layer of ammonia solution on to the liquid, which has previously been treated with silver nitrate solution. The precipitate will then appear as a yellow zone at the junction of the two liquids. On treating a solution of arsenic trioxide, to which a slight excess of silver nitrate has been added, with a moderate excess of ammonia, and heating the liquid to boiling point, metallic silver is precipitated, while the trivalent arsenic is converted into the pentavalent condition

7. **Cupric sulphate** does not produce a precipitate in an aqueous solution of arsenic trioxide; but on adding an *alkali hydroxide a yellowish-green precipitate of cupric hydrogen arsenite*, $CuHAsO_3$, is obtained. *This dissolves in potassium or sodium hydroxide solution, forming a blue solution*, from which, on boiling, a red precipitate of cuprous oxide is precipitated (*cf.* 8).

8. When arsenic trioxide is dissolved in excess of potassium or sodium hydroxide solution, or when a solution of an alkali arsenite is treated with potassium or sodium hydroxide, and a small quantity of a solution of *cupric sulphate* added, a *clear blue solution* is obtained, and this, when boiled, gives a *red precipitate of cuprous oxide;* the solution will contain arsenate ion. This reaction takes place readily and is highly sensitive, if too much copper solution is not used. If the red precipitate can no longer be recognised by transmitted light, it may still be seen quite distinctly, even when present in a minute quantity, by looking down into the test-tube from above. Important as is this reaction as a confirmatory test for trivalent arsenic in special cases, and in particular for distinguishing the latter from pentavalent arsenic, it is self-evident that it cannot be used as a direct proof of the presence of arsenic, since certain kinds of sugar and other organic substances can also precipitate cuprous oxide from solutions of cupric salts under the same conditions

9. Solutions of compounds of trivalent arsenic free from pentavalent arsenic do not give a precipitate with **magnesia mixture,**[1] or at most a very slight one after standing for a long time.[2]

10. On treating a hot solution of arsenic trioxide in strong hydro-

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[1] A solution of 55 grms. of crystallised magnesium chloride and 70 grms. of ammonium chloride in 350 c.c. of 8 per cent. ammonia solution and 650 c.c. of water.

[2] *Cf.* Sec. 92, 13, footnote.

chloric acid (sp. gr. 1·16 to 1·19) or sulphuric acid (sp. gr. 1·45 to 1·53) with a concentrated solution of potassium iodide, a red precipitate of *arsenic tri-iodide*, insoluble in the strong acid, is obtained (E. Srybel and Wikander, *Chem. Zeit.*, **26**, 50).

Antimony, when dissolved in sulphuric acid, also gives a precipitate. In hydrochloric acid solution, or when dissolved in sulphuric acid containing $\frac{1}{3}$ of its volume of hydrochloric acid, *antimony ion* does *not* give a precipitate with potassium iodide (Bressanin, *Zeitsch. anal. Chem.*, **52**, 70). Lead and tin also interfere with the precipitation from a solution in pure sulphuric acid, but not from a solution which has been treated with hydrochloric acid. Ferric chloride, free chloride, selenium, and mercury also interfere with the precipitation, but their influence may be eliminated by adding stannous chloride solution. If the potassium iodide is then rapidly added, Bettendorf's arsenic reaction (*cf.* 15), which always requires some time, will not yet have developed. According to Arnold and Mentzel (*Pharm. Zeit.*, **47**. 101), the reaction only takes place in hydrochloric acid solution, when the acid is of at least 22 per cent strength; otherwise the arsenic tri-iodide remains in solution. Aqueous solutions may be tested after the addition of a sufficient quantity of concentrated sulphuric acid. Substances which give precipitates with sulphuric acid or potassium iodide must not be present. Nitrate, nitrite, chlorate, chromate, permanganate, ferrocyanogen, and ferricyanogen ions must also not be present. Lead, silver, copper, and tin ions render the reaction untrustworthy.

The reaction is also suitable for the detection of arsenic when present in organic compounds (sodium cacodylate, arrhenal, atoxyl, salvarsan) In such cases the substance under examination is first heated with strong sulphuric acid, and the test then applied to the acid (Bressanin, *Zeitsch. anal. Chem* , **52**, 54).

11. On heating a solution which contains trivalent arsenic and has been treated with hydrochloric acid, with **absolutely bright copper strips or copper wire,** the copper becomes coated with an *iron-grey metallic deposit*, which, when it is abundant, separates in black scales. On heating the coated copper strips with ammonia solution, after removal of the free acid by washing, the deposit separates from the copper and subsides in spangles (Reinsch). It should be noted that these are not pure arsenic, but *copper arsenide*, Cu_5As_2 On heating the substance, previously dried or ignited in a current of air (whereby some arsenic trioxide escapes), in a current of hydrogen, an arsenic mirror is formed and relatively little arsenic escapes; alloys richer in copper are left (R. Fresenius, Lippert). On heating the washed and dried copper foil in a glass tube, lustrous crystals of arsenic trioxide are obtained, and may be easily

recognised by their characteristic form, especially when examined with a lens.

Only after arsenic has been detected in the deposited alloy is the reaction really characteristic of arsenic, since antimony and other elements, *e.g.* selenium, are similarly deposited under the same conditions upon copper, and a black film is also formed on the copper in the presence of sulphite ion In order to identify antimony and distinguish it from the other ions, Clarke (*Zeitsch. anal. Chem.*, **39**, 657) dissolves the deposit in hydrogen peroxide and sodium hydroxide solutions, and distils the solution after acidification with strong hydrochloric acid and addition of ferrous chloride (*cf.* end of 2). J. L. Howe and Paul S. Mertins (*Chem. Zentr.*, 1897, I., 78) recommend that the substance under examination should be boiled with thin copper foil in 16 per cent. hydrochloric acid for 15 minutes. The copper foil is then withdrawn, washed, dried, rolled up, and introduced into a sublimation tube, 5 cm. long, and not more than 0·5 cm. in diameter, which is then heated in an inclined position over a very small flame. If arsenic is present, a grey deposit will be formed on the copper, and this, when heated, will yield a sublimate of lustrous octahedra. Antimony also produces a deposit, although of a more violet colour, upon the copper, but the sublimate obtained on raising the temperature will not consist of lustrous octahedra. Organic substances do not interfere with the reaction, so that, *e.g.* animal organs may be tested directly for arsenic by boiling the material with hydrochloric acid and copper. If a solution under examination contains nitric acid, chlorate, or free chlorine, it must first be evaporated to dryness with hydrochloric acid, since otherwise the copper will be dissolved and no deposit obtained.[1]

12. *If an acid or neutral solution of arsenic trioxide or of an arsenate is brought into contact with* **zinc, water,** and **dilute sulphuric acid** or **hydrochloric acid,** *there is produced, in addition to hydrogen, the extremely poisonous gas, hydrogen arsenide,* AsH_3. (*The reaction must, therefore, be carried out with* **caution,** *and in a* **fume cupboard**). *The gaseous mixture burns with a pale blue flame. If a cold porcelain dish is held against the flame,* a *dark spot of arsenic* will be deposited upon it. *When the gas is passed through a tube heated at one place, an arsenic mirror will be formed in the part of the tube beyond the heated place.* This reaction, described by Marsh, and also by Liebig, is suitable for the detection of minute quantities of arsenic. For this purpose the apparatus shown in Fig. 43, or a similar apparatus, is used.[2] Here *a* represents the gas generating flask, *b* a bulb which

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[1] As an appendix to Reinsch's method, attention may be drawn to Hager's method, which depends upon the formation of spots upon brass foil (*Pharm. Zentralhalle*, **25**, 265, 443, 461 (1884).

[2] For details of other forms of Marsh's apparatus, reference may be made to Sec. 205: "Detection of metallic poisons."

retains water mechanically carried forward by the gas, and *c* a tube filled with cotton-wool and pieces of calcium chloride[1] in which the gas is dried. This is connected with *b* and *d* by means of rubber tubing, which has been boiled with sodium hydroxide solution The tube *d*, which is about 7 mm. in diameter (Fig 44), is composed of glass which is *free from lead* and *as free as possible* from arsenic, and is difficult to fuse. For very accurate tests the tube should be drawn out as shown in Fig. 43. A quantity, not too small, of zinc, which must be as pure as possible, and at all events absolutely free from arsenic,[2] is placed in the generating flask, and water is introduced through

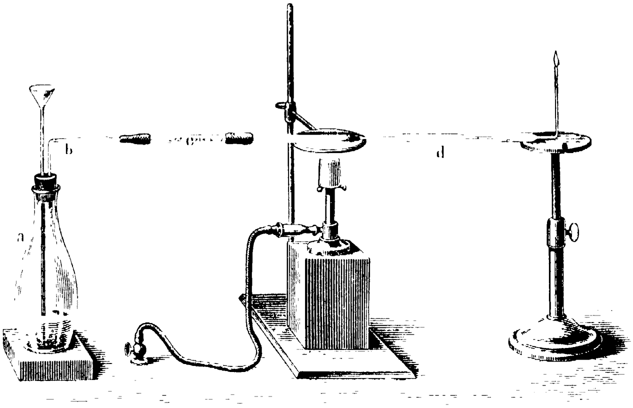

FIG. 43.

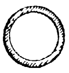

FIG. 44.

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[1] With regard to the behaviour of different drying agents, see Lockemann (*Zeitsch. angew. Chem.*, **18**, 425) This chemist recommends the use of large (about 1 cm.) crystals of calcium chloride when it is a question of very great accuracy

[2] Zinc, completely free from other metals, only liberates hydrogen slowly. If zinc containing copper (Hefti, *Diss. Zurich*, 1907) or zinc coated with copper (Lockemann, *Zeitsch. angew. Chem.*, **18**, 416) is used, a regular evolution of gas is at once obtained. The copper plating of the zinc is effected by shaking the granulated zinc with pure copper sulphate solution, decanting the liquid and washing the metal. The direct addition of a copper salt (as recommended by Mai and Hurt, *Zeitsch. anal. Chem.*, **43**, 557) may, according to Lockemann, lead to a slight loss of arsenic. The presence of iron in the zinc causes some of the arsenic to be retained in the flask. The zinc must, therefore, be tested for iron before use (Mai and Hurt, Lockemann; see also Parsons and Stewart, *Zeitsch. anal. Chem.*, **44**, 259). On the other hand, according to the same authorities, the presence of iron in the acid solution to be tested for arsenic does not have a disturbing influence (*Zeitsch. anal Chem.*, **47**, 728, and **50**, 597).

the funnel, until its level reaches the lower end of the funnel tube, after which a mixture of 1 part of pure concentrated sulphuric acid and 3 parts of water is gradually added, so that a regular and moderate current of hydrogen is developed. As soon as one can be certain that the whole of the air has been expelled from the apparatus,[1] the gas issuing from the tube *d* is lit (and before doing this it is advisable to make use of a safety tube, or to wrap a cloth round the flask as a protection against injury in case of a possible explosion) It is necessary in the first place to be absolutely certain that neither the zinc nor the sulphuric acid contains arsenic. For this purpose a porcelain basin is held horizontally in the flame, so that the latter is distributed over the surface. If the hydrogen contains arsenic, brown or blackish-brown spots of arsenic will be deposited on the porcelain. If this is not the case, and if greater accuracy is demanded of the test, the portion of the tube *d* shown in the illustration is heated to redness for some time, and a note taken whether a film of arsenic is deposited in the constricted portion of the tube. When it has been proved in this way that the hydrogen is pure, the liquid to be tested for arsenic is poured through the funnel, and the tube subsequently rinsed with a little water.[2] It is particularly advisable to introduce at first only a small amount of the liquid under examination Should a large quantity of a liquid containing a considerable amount of arsenic ions have been introduced, it is possible for the evolution of gas to be increased to such an extent that the test cannot be continued. If the liquid poured into the flask contains an oxide or a salt of arsenic, there is soon liberated, together with the hydrogen, *the extremely poisonous hydrogen arsenide*, which immediately causes the previously colourless flame to appear of a bluish tint. At the same time a white smoke of arsenic trioxide rises from the flame and will form a deposit on a cold surface If now a porcelain dish

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The use of platino-hydrochloric acid, which was formerly frequently recommended for the "activating" of zinc, may also cause a loss of arsenic. On this point, see also Harkins (*Chem. Zentr.*, 1910, I., 1848), various statements in the *Zeitsch. anal. Chem.*, **45**, 767 and 768, and Chapman and Law, *Zeitsch. anal Chem.*, **50**, 329. Struve (*Zeitsch. anal. Chem.*, **46**, 761) recommends the use of commercial zinc foil, and Carl Fischer (*Arb. Kaiserl. Gesundheitsamt*, **19**, 672) that of zinc rods. Kohn-Abrest recommends activated aluminium as a substitute for zinc (*Zeitsch. anal. Chem.*, **52**, 332), whilst A. Hébert recommends the use of sodium amalgam (*Ibid.*, 399).

[1] The test is applied by collecting the gas issuing from the tube in an inverted test-tube and applying a light. If the gas burns quietly and without a report it is free from air.

[2] Care must be taken when doing this that no air is introduced into the flask.

is held against the flame, the arsenic will be deposited upon it in the form of spots. Similar spots are also produced by antimony (*cf* Sec. 91, 12). With regard to their distinction from arsenic deposits, see Sec. 92, 8

If the tube *d* is *strongly heated at the place indicated in the illustration*, a *lustrous arsenic mirror* is formed *beyond this place*, either in front of or in the constricted part of the tube. This mirror is darker than an antimony mirror, and may also be easily identified by the fact that it may readily be expelled without previous melting in the current of hydrogen, and that the escaping (unlit) gas will then have, to a pronounced extent, the characteristic odour of arsenic. The mirror usually consists of two distinct zones, one brownish and the other blue-black (different modifications of arsenic. Thomson, *Zeitsch. anal Chem.*, **48**, 501) If the gas is burned while the mirror in the tube is heated, the flame will deposit spots of arsenic upon a porcelain basin even when there is only a very weak current of gas.

The presence of *mercury compounds*, especially mercuric chloride (Vitali, *Chem Zentralbl.*, 1905, I., 769) and of *fluorine ion* (W. van Rijn, *Ibid*, 1908, I, 1087), prevent or interfere with the detection of arsenic by means of Marsh's apparatus [1]

Sulphites, if present, yield hydrogen sulphide in the test, and this reacts with the hydrogen arsenide in the red-hot tube to form arsenic sulphide, which separates, sulphur, and hydrogen. If the hydrogen arsenide is present in excess, a mirror of arsenic is also produced (Smith, *Chem Zentr*, 1901, I., 279).

As a rule *arsenic sulphide* is not reduced in Marsh's test, and the presence of oxygenated or organic compounds of sulphur may, therefore, prevent the detection of arsenic by Marsh's test In like manner the presence of nitric acid prevents the reaction (Vournasos)

Arrhenal, $CH_3AsO(ONa)_2$, and also *cacodylic compounds*, yield black rings in the reduction tube in Marsh's apparatus The latter compounds also produce white vapour with an odour of garlic when the gas is burned, but the former do not produce such vapours Platino-hydrochloric acid prevents the formation of rings in the case of arrhenal (Vitali, *Zeitsch anal. Chem*, **50**, 599).

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[1] *Selenium compounds*, when present in any considerable quantity, yield a *red* deposit. In the presence of mere traces of selenium only a lustrous ring, which is difficult to distinguish from a slight arsenic deposit, is obtained. To test for selenium, if necessary, the original solution is saturated with hydrogen sulphide On then heating the liquid the precipitated sulphur agglomerates and turns brown in the presence of selenium. When carefully sublimed, the precipitate leaves a black residue, probably selenium sulphide (Meunier, *Chem. Zentr.*, 1916, II., 1069, and 1917, II., 193).

13. On heating a mixture of *dry sodium formate* with an arsenic compound to a temperature above 210°, the sodium formate is converted into oxalate, hydrogen and also hydrogen arsenide being formed in the process. The latter may be identified by one of the methods described in 12 or 14, or Sec. 92, 9 (Vournasos, *Ber.*, **43**, 2264). If the test is to be made by Marsh's method, the following procedure is, in our experience, suitable for the purpose: The sodium formate is heated until it begins to melt, and the dehydrated salt is powdered. A little sodium formate thus freshly dried is introduced into a piece of combustion tubing about 20 cm. long, which is fused together at one end, and then, but separated by a space, there is added a mixture of the substance under examination with at least 5 parts of the freshly dried sodium formate. Finally, the tube, a portion of which must always be left clear, is closed by a cork through which is passed a Marsh's tube. The tube must be charged in such a way that it is at least half empty. This can be done by bending a piece of paper, so as to form a channel, placing the pure sodium formate and the mixture containing the substance under examination on the paper with a space between them, introducing the paper channel into the horizontal tube, turning the latter about 180° on its axis, and withdrawing the paper. On now heating the pure sodium formate, care being taken to prevent too much frothing, the liberated hydrogen (or the carbon dioxide produced when the substance is more strongly heated), expels the air from the tube. On then heating the mixture under examination hydrogen arsenide is produced when arsenic is present, in the same way as in Marsh's test, forming a mirror when the narrow tube is heated, and giving a flame which produces spots on cold surfaces, and also acts upon silver nitrate or mercuric chloride, as described in 14, or in Sec. 92, 9. Sulphur compounds and nitrates do not interfere with the test. (Advantage over Marsh's method.) Antimony compounds are reduced by sodium formate, but no hydrogen antimonide is liberated when the temperature does not exceed 800°; if, therefore, the temperature is kept below 400° the formation of a mirror indicates the presence of arsenic (Vournasos).

Naturally, a blank test must be made to prove that the sodium formate used does not itself produce a mirror, and also does not give a tarry deposit.

14. *If hydrogen containing hydrogen arsenide is produced by any method* (*cf.* 12 and 13), *and the gas conducted into a solution of* **silver nitrate,** *silver will separate*, while arsenious acid will remain in the solution. If the gas is brought into contact with **filter paper impregnated with silver nitrate solution,** a yellow stain (Gutzeit) is produced if the solution was concentrated, and a black one if it was dilute.[1] The test is made, *e.g.* by treating a granule of *zinc* with *sulphuric acid* in a test tube, and introducing the substance under examination. A wad of cotton-wool is put into the mouth of the

[1] For further details, see Sec. 92, 9 (*e*)

test-tube, and over it is placed the filter paper, which has been impregnated with the silver solution. Hydrogen phosphide, hydrogen antimonide, and hydrogen sulphide interfere with the reaction. With regard to the difference in the behaviour of arsenic and antimony, see Sec. 92, 9.[1]

15. On treating about 5 c.c. of **fuming hydrochloric acid** with a few drops of **stannous chloride solution,** and adding *a few drops of a solution of arsenic trioxide or an arsenite, reduction takes place*, and a *brownish-black precipitate of arsenic* is obtained (Bettendorf). (Antimony compounds are not reduced under the same conditions.) The reaction, which takes place slowly in the cold, but rapidly on heating,[2] is very sensitive, but is only obtained when excess of *fuming* hydrochloric acid is present. If the hydrochloric acid has too low a specific gravity, the precipitation is either incomplete or does not take place at all. (Only the arsenious ion present in concentrated hydrochloric acid solution is reduced, not the arsenite ion, which is present in the solution diluted with water, *cf.* Sec. 89, 2.) If frequent tests for arsenic are to be made by this method, it is convenient to have a solution of stannous chloride in highly concentrated (38 per cent.) hydrochloric acid ready for the purpose. Instead of using stannous chloride, the substance may also be heated in a test-tube with 20 to 40 mgrms. of tin and 10 to 12 drops of concentrated hydrochloric acid (Ferraro and Carrobio, *Zeitsch. anal. Chem.*, **46**, 177). Obviously it is still an essential condition that the liquid should contain strong hydrochloric acid. With regard to this reaction, see also *Zeitsch. anal. Chem.*, **36**, 215; **39**, 11, and especially **55**, 358, where, too, details are given as to the sensitiveness of the test.

16. On treating a solution of arsenic trioxide or an arsenite with an equal or double volume of *concentrated hydrochloric acid* and some solid *sodium hypophosphite*, and heating the liquid to boiling point, a brownish-black precipitate, similar to that described in 15, separates when the quantity of arsenious ion is not too small. In the presence of a very small amount of arsenious ion only a *yellowish-brown* to *brown coloration* of the liquid is obtained, even after heating

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[1] Purin and oxypurin also cause black stains to appear in the absence of arsenic (Dilling, *Zeitsch. anal. Chem.*, **53**, 278).

[2] L. W. Winkler has shown that even in the presence of sulphates the liquid can be heated without separation of stannous sulphide taking place (which other authorities have stated to occur) (*Zeitsch. angew. Chem.*, **26**, 113; *Zeitsch. anal. Chem.*, **55**, 80). Sulphuric acid may be reduced to hydrogen sulphide, however, and the latter may interfere with the reaction, *e.g.* in the presence of bismuth (Peters, *Handb. anal. Praxis*, II., 62).

it for a long time. The addition of a small crystal of potassium iodide materially increases the sensitiveness of the reaction, but cannot be used in the presence of substances which give precipitates with potassium iodide, or liberate iodine from that salt (Loof, Thiele).[1]

17. If *arsenites*, *arsenic trioxide*, or *arsenic trisulphide* are *fused* with **a mixture of 3 parts of dry sodium carbonate and 1 part of potassium cyanide,** *the whole of the arsenic* is reduced, and also the cation present in the arsenite, when it is reducible, while the oxygen converts part of the potassium cyanide into cyanate. Potassium thiocyanate is formed in the reduction of arsenic trisulphide. *Whilst the whole of the arsenic is volatilised during the reduction of arsenic trioxide and sulphide*, and is obtained as a *mirror* when the reduction is carried out in a suitable apparatus, arsenites only yield a mirror when their cation is either not reduced at all, or is reduced to a metal arsenide, which, when heated, loses part or all of its arsenic. This method of *reducing arsenic compounds with potassium cyanide*, devised by R. Fresenius and L. von Babo, may be especially recommended for its simplicity, the certainty with which it will detect very minute quantities of arsenic, and the cleanliness with which it can be applied. *It is especially suitable for the direct preparation of arsenic from arsenic sulphide, for which purpose it unquestionably excels all other methods in simplicity and accuracy.*

The process is preferably carried out in an *atmosphere of carbon dioxide*, so as to prevent the oxidation of arsenic, when present in only small amount, by the atmospheric oxygen. Since ordinary glass at the present time almost invariably contains arsenic, and may thus, when brought into contact with a mixture of potassium cyanide and sodium carbonate in a state of fusion, cause a mirror to be formed, even when arsenic is absent from the mixture,[2] its use must be avoided. For this reason the original apparatus of R. Fresenius and L. von Babo should be modified as represented in Fig. 45.

Here *ab* represents a Kipp's apparatus charged with pieces of marble and pure dilute hydrochloric acid for the evolution of carbon dioxide. *c* a washing flask, which contains pure concentrated sulphuric acid to dry the carbon dioxide, and *d* is a tube of lead-free glass of

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[1] The reaction described by R. D. Staddon for the detection of very small amounts of arsenic, like those given in 15 and 16, is also based upon a reduction of the compound to elementary arsenic. On adding to the solution under examination 0·5 to 2 grms. of commercial sodium hydrosulphite, $Na_2S_2O_4$ (*cf.* footnote to heading of Sec. 102), a finely pulverulent metallic precipitate is obtained. *Antimony compounds* behave in the same way. Arsenic is soluble, whilst antimony is insoluble, in sodium hypochlorite solution. See, however, Sec. 92, 8, footnote (*Chem. Zentr.*, 1912, II., 1885.)

[2] *Cf.* W. Fresenius, "Arsenic in glass as a source of error in the detection of arsenic" (*Zeitsch. anal. Chem.*, 22, 397)

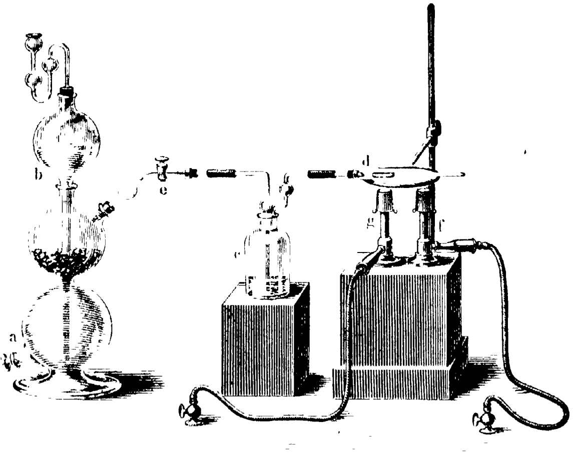

FIG. 45.

high fusing point. Fig. 46 represents this tube one half of its natural size. The tube must be of such a width that the porcelain

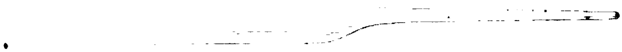

FIG. 46.

boat, intended to receive the mixture to be heated (and shown in its actual size in Fig. 47) can just be introduced into it.

When the apparatus has been prepared and is filled with carbon dioxide, the arsenic compound to be reduced (which must be absolutely dry) is ground up with 12 parts of a mixture (entirely free from arsenic) of 3 parts of sodium carbonate and 1 part of potassium cyanide, the powder placed in the porcelain boat, and the latter introduced into the reduction tube in the position shown in Fig. 48. The tube is then connected with the washing flask, a moderate

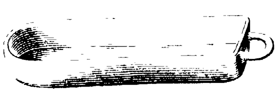

FIG. 47.

current of carbon dioxide admitted by turning the tap *e* (Fig. 45), and the mixture carefully dried by gently heating the boat and the whole length of the tube by means of a lamp. When all condensed water has been expelled from the tube, the speed of the current of gas is reduced so that the individual bubbles pass through the sulphuric acid at intervals of about a second, and the wider portion of the tube is heated to redness at the point where it begins to contract, by means of the burner *f*. When this temperature is reached the boat is heated by means of the burner *g*. moderately at first, to prevent spurting of the fused mass, and then more strongly, until the whole of the arsenic has been expelled. Should an arsenic deposit form in the wider portion of the tube, this, too, should be heated progressively up to the narrow portion. Practically the whole of the arsenic will then be found as a metallic mirror (Fig. 48) beyond the portion of the tube which is still continuously heated by the burner *f* whilst a small fraction of it escapes from the point of the tube and produces an odour of garlic in the air. Finally, the point of the tube may be fused together and the mirror carefully volatilised by heating the point of the tube, so that the arsenic is deposited nearer to the wider portion, whereby it acquires a particularly fine and distinctive metallic appearance. In this way a perceptible mirror may be obtained from as little as $\frac{1}{100}$ mgrm. of arsenious anhydride.[1]

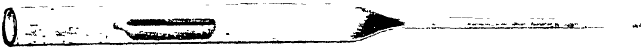

FIG. 48.

Antimony sulphide, or other antimony compounds, do not give a metallic mirror when treated in this way. But the current of carbon dioxide must not be replaced by a current of hydrogen if the formation of antimony mirrors is to be avoided.

18. If arsenic trioxide or an arsenic compound is exposed to the *inner blowpipe flame* on charcoal, the characteristic *odour*, recalling that of garlic, which has been frequently mentioned, will be diffused; this odour is produced by the yellow modification of arsenic, and enables very minute traces thereof to be detected.

19. A *biological method* of detecting very small amounts of arsenic has been described by Gosio (*Zeitsch. anal. Chem.*, **39**, 479), F. Abba (*Ibid.*,); Abel and Buttenberg (*Ibid.*, **41**, 137); Morpurgo

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[1] *Cf.* W. Fresenius: "The correct method of applying the Fresenius-Babo test for arsenic, and its sensitiveness" (*Zeitsch. anal. Chem.*, **20**, 531).

and Brunner (*Chem. Zentr.*, 1898, II., 505). It is based upon the fact that certain *mould-fungi*, when grown on culture media containing arsenic, produce *gases* (probably mixtures of arsines and hydrogen arsenide), *which may be recognised by their garlic-like odour.* (The method is also applicable to atoxyl. B. Galli-Valerio, *Zeitsch. anal. Chem.*, **51**, 153.) The substance is either introduced in the form of a small strip (carpet, etc.) into a hole made in the middle of a slice of potato (Abba), or is mixed in the form of a powder or solution with ground-up potato (Gosio) or bread-crumbs (Abel and Buttenberg), then sterilised, inoculated with *Penicillium brevicaule*, kept for 24 to 72 hours in an incubating oven, and its odour then tested. The presence of antiseptic agents such as mercuric chloride, etc., and also of free acids, prevents the reaction. Acid liquids must, therefore, be neutralised. Antimony, phosphorus, and bismuth compounds do not yield odorous gases when treated in this way, but selenium compounds yield gases with an odour recalling that of mercaptan, and tellurium compounds gases with a garlic-like odour (Maasen, *Zeitsch. anal. Chem.*, **43**, 136).[1]

20. With regard to the *microchemical detection* of trivalent arsenic, see Haushofer, *Mikroskopische Reaktionen*, p. 15; Behrens-Kley, *Mikroskopische Analyse*, 3rd ed., p. 131; Emich, *Zeitsch anal. Chem.*, **32**, 167; Justus, *Ibid.*, **46**, 178; Schoorl, *Ibid.*, **47**, 370, 381; Sjollema, *Ibid.*, 726; Denigès, *Ibid.*, **48**, 395; Nieuwlands, *Ibid.*, **50**, 598; Hartwich and Toggenburg, *Chem. Zentr.*, 1909, I., 580.

SEC. 90.

(β) Pentavalent Arsenic.

1. *Arsenic pentoxide*, As_2O_5 (arsenic anhydride), is a colourless or white, vitreous, fusible mass, which dissolves slowly in cold and rapidly in hot water, and when strongly ignited is decomposed into oxygen and arsenic trioxide. On allowing the solution to stand at a somewhat low temperature, it yields *arsenic acid* (ortho-arsenic acid) containing water of crystallisation, $2H_3AsO_4 + H_2O$, in colourless crystals, which deliquesce in moist air, and lose their water of crystallisation at 100°. At 180° *pyro-arsenic acid*, $H_4As_2O_7$, is obtained; at 206° meta-arsenic acid, $HAsO_3$; whilst arsenic pentoxide is produced near the ignition temperature. All the arsenic acids

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[1] For details of other lower organisms having a similar action, see *Zeitsch. anal. Chem.*, **43**, 657; for the detection of arsenic normally present in the organs of the body, see *Ibid.*, **44**, 724; further, W. Scholtz, *Ibid.*, **45**, 666; Pool, *Chem. Zentr.*, 1912, II., 1744; Huss, *Ibid.*, 1911, I., 801; Klason, *Ibid.*, 1911, II., 1247.

dissolve in water, forming ortho-arsenic acid. The arsenic acids and arsenic pentoxide are poisonous.

2. The *arsenates* correspond to the acids in composition. Hence they are known as *arsenates* (ortho-arsenates), *pyro-arsenates*, and *meta-arsenates*. The ortho-arsenates are either neutral, or mono-acid or di-acid salts. The alkali arsenates and dihydrogen arsenates (di-acid salts) of the alkaline earth metals are soluble in water, and nearly all the other arsenates dissolve in hydrochloric or nitric acid The anhydrous arsenates of non-volatile metals are not decomposed on ignition.

A solution of arsenic pentoxide or of an arsenate in hydrochloric acid may be boiled for a long time without arsenic trichloride volatilising, if it does not contain too much hydrochloric acid. Only when the residue consists of about equal parts of hydrochloric acid of sp. gr. 1·12 and of water do traces of arsenic trichloride escape with the hydrogen chloride. *When a solution containing pentavalent arsenic is repeatedly distilled with concentrated hydrochloric acid and ferrous chloride* (*or cuprous chloride or potassium iodide or bromide*), *the whole of the arsenic is obtained as trichloride* (together with iodine or bromine, as the case may be) *in the distillate*. (Distinction from antimony and tin compounds) (Emil Fischer, *Liebig's Ann.*, **208**, 182 ; *Zeitsch. anal. Chem.*, **21**, 266 ; Gooch and Hodge, *Zeitsch anorg Chem.*, **6**, 268 ; *Zeitsch. anal. Chem.*, **34**, 90 ; Gooch and Phelps, *Zeitsch. anorg. Chem.*, **7**, 127.[1])

3. **Hydrogen sulphide** does *not* precipitate the ions of pentavalent arsenic from *alkaline* and *neutral solutions*, and *at first* produces *no precipitate in the cold in moderate acid solutions*. After the solutions have stood for some time some separation of colloidal arsenic pentasulphide and sulphur takes place, and there is a *partial reduction* of the arsenate ion to the trivalent arsenic ion, *which is followed by the precipitation of yellow arsenic pentasulphide and arsenic trisulphide* This process continues uninterruptedly *until finally the whole of the arsenic has been precipitated* (Brauner and Tomicek, Thiele). *Hydrogen*

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[1] Friedheim and Michaelis (*Zeitsch. anal. Chem.*, **39**, 708) recommend distillation with methyl alcohol in a current of hydrogen chloride for cases where it is desired that the residue should not contain any foreign matters derived from the reducing agents. These chemists have given this method as being especially suitable for the separation of arsenic ion from vanadium and molybdenum ions. Friedheim, Decker, and Diem give the preference to potassium iodide and hydrochloric acid as reagent (*Zeitsch. anal. Chem.*, **44**, 678). Jannasch and Seidel use *hydrazine salts* in the presence of potassium bromide (*Ber.*, 43, 1218) for this purpose, whilst, according to Ebler, *hydrazine bromide* is preferable (*Zeitsch. anal. Chem.*, **50**, 603). *Cf.* also Billeter, *Ibid.*, **54**, 190.

sulphide speedily precipitates arsenic pentasulphide from strongly (hydrochloric) acid solutions (containing at least 2 parts of concentrated hydrochloric acid of sp. gr. 1·12 to 1 part of water). (Fr. Neher.)

If hydrogen sulphide is conducted into a moderately acid arsenate solution heated to about 70°, *arsenic pentasulphide* is invariably obtained when the hydrogen sulphide is in large excess; otherwise a *mixture of arsenic pentasulphide, arsenic trisulphide*, and *sulphur.* On adding sulphur dioxide or sodium sulphite and hydrochloric acid to a solution of arsenic acid or an arsenate, reduction of the pentavalent to trivalent arsenic takes place (most rapidly on heating the liquid), whilst sulphate ion is simultaneously formed. On then adding hydrogen sulphide, the whole of the arsenic is immediately precipitated as arsenic trisulphide.

Atoxyl, which contains pentavalent arsenic in complex combination, $NH_2 C_6H_4.AsO OH.ONa + 4H_2O$, does not give any precipitate with hydrogen sulphide.

The precipitates produced by hydrogen sulphide in solutions of pentavalent arsenic behave towards alkalis, alkali sulphides, and acids, on fusion with sodium nitrate and carbonate, and when heated with ammonium nitrate and chloride, in the same way as those obtained from solutions of trivalent arsenic.

Ammonium thioacetate behaves towards hydrochloric acid solutions of arsenates in the same way as towards arsenite solutions (*i.e.* it produces a turbidity in the cold, and immediate and complete precipitation of arsenic trisulphide on heating the liquid).

Sodium thiosulphate completely precipitates ions of pentavalent arsenic as sulphide from acid solutions (although somewhat less readily than those of trivalent arsenic).

4. **Ammonium sulphide,** added to neutral and alkaline solutions of arsenates, causes the *formation of sulpho-arsenate*, which remains in solution, *e.g.* $Na_3AsO_4 + 4(NH_4)_2S + 4H_2O = Na_3AsS_4 + 8NH_4OH$. On adding *acid* this anion is decomposed, and *arsenic pentasulphide* (*not* a mixture of arsenic trisulphide and sulphur) is precipitated. The precipitation takes place more rapidly from cold moderately acid solutions than that produced by hydrogen sulphide. It is promoted by heat.

5. **Silver nitrate** *produces in solutions of arsenic acid and alkali arsenates a very characteristic reddish-brown precipitate of silver arsenate*, Ag_3AsO_4, *which is readily soluble in dilute nitric acid and ammonia solution, and is also dissolved to some extent by ammonium*

nitrate solution.[1] If, therefore, the precipitate is dissolved in a little nitric acid, and a little dilute ammonia solution poured on to the solution, the precipitate separates at the *zone of contact* of the liquids, and *forms a ring*. The addition of a little sodium nitrate increases the sensitiveness of this reaction. If, however, a little of the precipitate is dissolved in a very large amount of hydrochloric acid, the precipitate frequently will not be formed again on neutralising the liquid with ammonia, owing to the solvent action of the ammonium nitrate. An ammoniacal solution of silver arsenate does *not* give a deposit of metallic silver when boiled. (Distinction of arsenate ion from arsenite ion.)

6. *Cupric sulphate* does not produce a precipitate in an aqueous solution of arsenic. On the addition of an alkali hydroxide a bluish-green precipitate of cupric arsenate is formed. When more potassium or sodium hydroxide is added this precipitate becomes pale blue without dissolving. When the liquid is boiled *cuprous oxide* is not precipitated. (Distinction of arsenate ion from arsenite ion.) (Atoxyl solutions give a crystalline green precipitate with cupric sulphate solution; it is soluble in acids and ammonia solution.)

7. On heating a dilute solution of arsenic acid (or an arsenate), which has been treated with a little hydrochloric acid, with *metallic copper*, the latter remains quite bright (Werther, Reinsch); if, however, the solution is treated with twice its volume of concentrated hydrochloric acid and then heated, the copper becomes coated with a grey deposit in the same way as in the case of trivalent arsenic. Under these conditions the reaction is as sensitive as when arsenite ion is present (Reinsch). Atoxyl also gives the reaction, although slowly (Gadamer).

8. On adding a solution of *arsenic acid* or of an *arsenate*, soluble in water, to a clear mixture of **magnesium chloride** (or *magnesium sulphate*), **ammonium chloride**, and not too little **ammonia solution** (magnesia mixture), a crystalline precipitate of *ammonium magnesium arsenate*, $MgNH_4AsO_4+6H_2O$, is obtained immediately with concentrated solutions, after some time with dilute, and after a long time with very dilute solutions. On dissolving a little of the precipitate in a drop of nitric acid in a clock glass, adding a little silver nitrate solution, and stirring the liquid with a glass rod which has been dipped in ammonia solution, a brownish-red precipitate of silver arsenate will be obtained. When hydrogen sulphide is conducted

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[1] Atoxyl gives with silver nitrate a white precipitate, which is soluble in nitric acid and ammonia solution (Gadamer, *Zeitsch. anal. Chem.*, **47**, 332).

into a hot solution of ammonium magnesium arsenate in hydrochloric acid, a yellow precipitate is obtained. (Distinction of ammonium magnesium arsenate from the corresponding phosphate.)

9. On adding *a small quantity* [1] of a solution of *arsenic acid* or of an arsenate to a few c.c. of a solution of **ammonium molybdate** in **nitric acid,** *no* precipitate is formed *in the cold*, even after the liquid has been allowed to stand for a long time. If, however, the liquid is heated, preferably not much above 70°, a *bright yellow* [2] *precipitate of ammonium arsenomolybdate* separates; under the microscope this is seen to consist of stellar groups of needles. Ammonium arsenomolybdate is soluble in ammonia solution. On adding to the resulting colourless solution the magnesia mixture mentioned in 8, the reaction there described is obtained.

10. Compounds of pentavalent arsenic behave in the same manner as those of trivalent arsenic towards *stannous chloride* in the presence of fuming hydrochloric acid,[3] *sodium hypophosphite*, and hydrochloric acid, *zinc* in the presence of sulphuric acid,[4] and *potassium cyanide*, and also *before the blowpipe*. When arsenic is reduced in a platinum basin by means of zinc, the platinum is *not stained black*. (Distinction from antimony.)

11. With regard to the *microchemical detection* of pentavalent arsenic, see Haushofer, *Mikroskopische Reaktionen*, p. 15; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 131; Denigès, *Zeitsch. anal. Chem.*, **53**, 405.

SEC. 91

(c) Antimony, Sb. 120·2.

1. *Antimony* is *trivalent* and *pentavalent*, and tetravalent compounds are also known. Metallic antimony is bluish-white, lustrous, hard, brittle, melts at 630°, and is volatile at a very high temperature (boiling point 1300°). Its specific gravity is 6·5 to 6·7. Nitric acid oxidises antimony, the dilute acid converting it almost quantitatively into trioxide, whilst by increasing the concentration, a correspondingly larger amount of pentoxide (antimonic anhydride) is formed,

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[1] An excess of arsenate solution must be avoided, since the yellow precipitate is soluble in alkali arsenate solution.

[2] A white or only faintly yellow precipitate, which is formed if the liquid is heated too strongly and consists of precipitated molybdic acid, is obviously no proof of the presence of arsenate ion.

[3] In the case of arsenates, Bettendorf's reaction takes place more slowly, especially when it is a question of only *small* amounts of arsenate. Atoxyl does not give Bettendorf's reaction (Gadamer).

[4] Atoxyl also yields hydrogen arsenide (Gadamer).

and boiling concentrated acid oxidises it almost completely to pentoxide. The product of neither of these oxidation stages is absolutely insoluble in nitric acid. Hence the acid filtrates from the precipitates invariably contain traces of antimony. Antimony is readily soluble in nitric acid in the presence of tartaric acid Hydrochloric acid, even when boiling, does not attack antimony when air is excluded. *Aqua regia* dissolves it readily. The solution will contain trichloride, $SbCl_3$, or pentachloride, $SbCl_5$, according to the duration of the action and the concentration. According to Henz (*Zeitsch. anorg Chem.*, **37**, 1; *Zeitsch. anal. Chem.*, **46**, 593), hydrochloric acid to which bromine has been added is a still more suitable solvent for antimony.

2. *Antimony trioxide* (antimonous oxide), Sb_2O_3 or Sb_4O_6, occurs either as white, lustrous, acicular crystals, or as a white powder, according to the method of preparation It melts at a low ignition temperature in the absence of air, and volatilises without decomposition at a higher temperature. It is insoluble in water, is readily soluble in hydrochloric and tartaric acids, and only very sparingly soluble in nitric acid. On boiling it with hydrochloric acid (free from chlorine) and potassium iodide (free from iodate) no separation of iodine takes place (Bunsen) When fused with potassium cyanide, antimony trioxide is readily reduced.

The *hydroxides* of trivalent antimony are white; they possess both a slightly acid and slightly basic character, corresponding to antimonous ion, $Sb^{\cdot\cdot\cdot}$, antimonyl ion, $SbO^{\cdot}$, and antimonite ion, SbO'_2. They gradually change, even under water, owing to the liberation of water, into antimony trioxide.

3. *Antimony pentoxide* (antimonic anhydride), Sb_2O_5, is pale yellow. Three acids correspond to it, *viz.* orthoantimonic acid, H_3SbO_4, pyroantimonic acid, $H_4Sb_2O_7$, and meta-antimonic acid, $HSbO_3$. These acids are white. Antimony pentoxide, as also the antimonic acids, redden moist litmus paper; they are scarcely soluble in water, and almost insoluble in nitric acid, but dissolve fairly readily in hot concentrated hydrochloric acid to form a solution, which contains antimony pentachloride, $SbCl_5$, and becomes turbid on the addition of water. On boiling antimony pentoxide with hydrochloric acid and potassium iodide there is a separation of iodine, which, in the presence of hydriodic acid, dissolves to form a brown solution (Bunsen). When ignited antimony pentoxide loses oxygen and is converted into infusible antimony tetroxide, Sb_2O_4 Of the salts of ortho-, pyro- and meta-antimonic acids, only the

potassium salts are soluble in water; the corresponding antimonic acids are precipitated from these solutions by acids. Sodium chloride precipitates disodium dihydrogen pyroantimonate from a solution of dipotassium dihydrogen pyroantimonate, $Na_2H_2Sb_2O_7$. (See 29, 3)

4 The *salts of trivalent antimony* (antimonous salts) with volatile acids are decomposed on ignition, whilst the haloid salts volatilise readily and without decomposition. The soluble neutral antimonous salts redden litmus in consequence of hydrolysis, when treated with a large amount of water they yield insoluble basic salts and acid solutions containing antimonous ion. Thus water, when added in large proportion to a solution of antimony trichloride in hydrochloric acid, precipitates a voluminous white precipitate of basic antimonous oxychloride (powder of algaroth), $2(SbOCl),Sb_2O_3$, which becomes heavy and crystalline after some time. Tartaric acid readily dissolves the precipitate; hence it prevents the precipitation if added prior to the addition of water. This behaviour distinguishes antimonous oxychloride, SbOCl, from bismuthyl salts formed under the same conditions. Some of the basic salts contain the monovalent cation, antimonyl, SbO. Tartar emetic, $C_4H_4O_6K(SbO)$, and many other antimony compounds are doubtless to be regarded as simple basic salts, but they might also be considered to be compounds with complex anions containing antimony. The addition of a little hydrochloric acid to solutions of tartar emetic and analogous compounds produces a white precipitate of antimonous oxychloride, which dissolves on the addition of more hydrochloric acid

$$C_4H_4O_6K(SbO) + HCl = C_4H_5O_6K + SbOCl$$

5 **Hydrogen sulphide** *precipitates antimony incompletely from neutral solutions of trivalent antimony, and not at all, or at all events not completely, from alkaline solutions, but from acid solutions*, if the quantity of free acid (mineral acid) is not too great, *it precipitates it quantitatively as amorphous orange-red antimony sulphide*, Sb_2S_3. The precipitate is readily dissolved by *potassium* or *sodium hydroxide solution*, and by *solutions of alkali sulphides*, especially when they contain polysulphides, but is only slightly soluble in ammonia solution (distinction from antimony pentasulphide), and, when free from antimony pentasulphide, practically insoluble in ammonium hydrogen carbonate solution. It is *insoluble in cold dilute acids*, and also in alkali hydrogen sulphite solutions. *Concentrated hydrochloric acid* of sp. gr. 1·18 dissolves it, *even in the cold*, with the evolution of hydrogen

sulphide, whilst it is *soluble even in hydrochloric acid of sp. gr.* 1 12 when heated.

When heated in the absence of air (*e.g.* in a current of carbon dioxide) or even beneath a liquid, the *orange-red antimony trisulphide* is converted into *black* trisulphide. In the presence of air the precipitate is converted into a mixture of antimony tetroxide with antimony sulphide (trisulphide or pentasulphide). On boiling a solution of antimony trisulphide in potassium hydroxide or sulphide solution with *bismuthous oxide*, bismuth sulphide is formed, while antimonite ion remains in solution; if the alkaline solution is boiled with *cupric oxide*, cuprous sulphide will be produced, and the alkaline solution will then contain pyroantimonate ion. By igniting antimony sulphide with *sodium nitrate*, sodium sulphate and *sodium* pyroantimonate are obtained. When heated in a current of *chlorine* or ignited with a mixture of 5 parts of *ammonium chloride* and 1 part of *ammonium nitrate*, antimony sulphide volatilises completely, being decomposed in the process. If the latter operation is carried out in a tube fused together at the bottom, or in a current of air, the antimony will be found as trichloride in the sublimate. On fusing antimony sulphide with *potassium cyanide*, *elementary antimony* and potassium thiocyanate will be obtained. If the operation is carried out in a small tube, the lower part of which has been blown into a bulb, or in a current of carbon dioxide (*cf.* Sec. 89, 17), *no sublimate* of antimony will be obtained. If, however, the antimony sulphide is mixed with sodium carbonate or with sodium carbonate and potassium cyanide, and heated in a *current of hydrogen* (*cf.* Sec. 89, end of 17), an antimony mirror will be formed in the tube immediately beyond the place where the mixture was placed.

Hydrogen sulphide precipitates *antimony pentasulphide*, Sb_2S_5, mixed with antimony trisulphide and sulphur, from a solution of *antimony pentoxide*. The precipitate dissolves readily in a hot solution of sodium hydroxide or ammonia, very sparingly in cold ammonium hydrogen carbonate solution, and readily in boiling concentrated hydrochloric acid, with the evolution of hydrogen sulphide and separation of sulphur.

6. **Ammonium sulphide** produces an *orange-red precipitate of antimony trisulphide* in solutions containing trivalent antimony. The precipitate dissolves readily in excess of the precipitant, especially when *the latter contains polysulphide*. Acids precipitate antimony pentasulphide (Sb_2S_5) from this (polysulphide) solution.

Its orange colour, however, usually appears paler under these conditions, owing to the presence of admixed sulphur.

7. *Sodium thiosulphate* precipitates *antimony sulphide* or, under suitable conditions, red "antimony vermilion," Sb_2S_2O, *i.e.* a mixture of Sb_2S_3, with varying small quantities of Sb_2O_3. This may be very readily obtained by treating a solution of sodium thiosulphate with an aqueous solution of sulphur dioxide (whereby the solution becomes yellow), adding a small quantity of a solution containing trivalent antimony, and heating the liquid to boiling point. The liquid first becomes turbid owing to the separation of sulphur, and the antimony is then precipitated as red antimony vermilion.

8. **Potassium hydroxide**, and also **sodium hydroxide**, **ammonia**, **sodium carbonate**, or **ammonium carbonate**, produce a voluminous white precipitate of antimony hydroxide in solutions of antimony trichloride or of simple antimony salts, but less completely and only after some time in solutions of tartar emetic or analogous compounds; this precipitate, in accordance with its slightly acid character, dissolves fairly readily in excess of potassium or sodium hydroxide solution, but is practically insoluble in ammonia solution, and only dissolves in sodium carbonate solution when heated.

9. Metallic **zinc** and, in similar manner, metallic **tin** (distinction from tin (Pieszczek)) or *magnesium*, precipitate *elementary antimony as a black powder from all solutions of antimony salts*, if they contain no free nitric acid. If a few drops of a solution of an antimony salt containing a little free hydrochloric acid are placed in a *platinum basin* (or the inside of a platinum crucible lid), and a small fragment of zinc or tin introduced into the solution, antimony separates, while hydrogen containing hydrogen antimonide is evolved. *The part of the platinum covered by the liquid becomes brown or black*, even in the case of very dilute solutions. This reaction is as sensitive as it is characteristic. The deposited antimony dissolves in hydrochloric acid of sp. gr. 1·12, speedily even in the cold when the stain is very slight, but slowly and only after heating when it is pronounced; on heating the deposit with nitric acid containing a little tartaric acid it dissolves immediately.

10. On heating a *solution of an antimony salt* containing a little hydrochloric acid with bright **iron,** *e.g.* a small iron rod, the whole of the antimony soon separates *in the form of heavy black flakes*. (Distinction from tin.)

On treating (in Reinsch's test) a solution containing antimony ions with sufficient hydrochloric acid to give a solution containing about 16 per cent. of that acid, and boiling the liquid with thin strips of bright *copper foil*, the antimony is precipitated on the copper in the form of a violet deposit. When the copper strip is washed, dried, rolled up, and heated in a glass tube, a (non-crystalline) sublimate is obtained, although only after strong heating The precipitation also takes place in the presence of organic substances (Howe and Mertins, *Chem Zentr.*, 1897, I , 78).

11. *On treating a solution of trivalent antimony in potassium or sodium hydroxide solution* (obtained by precipitation with alkali hydroxide and dissolving the precipitate in excess of the reagent) with *silver nitrate*, there is produced, in addition to a greyish-brown precipitate of silver oxide, a deep black precipitate which was formerly considered to be silver suboxide. On then adding ammonia solution in excess, the silver oxide dissolves, whilst the black precipitate remains undissolved (H. Rose). According to the investigations of Pillitz, this precipitate is a mixture of *antimony* and *silver* in variable proportions, and possibly also contains a chemical compound of the two metals. This extremely sensitive reaction affords a particularly good means of detecting trivalent antimony in the presence of pentavalent antimony.

12. If a solution containing antimony ions is introduced into a flask in which *hydrogen is being evolved from pure zinc and dilute sulphuric acid*, the zinc, in addition to causing the evolution of hydrogen, also effects a reduction of the antimony compound *Antimony thus separates in metallic form* (see 9), but at the moment of separation part of it also combines with the hydrogen to form gaseous *hydrogen antimonide*, SbH_3. If this operation is carried out in the apparatus used for Marsh's test for arsenic (See 89, 12), and a light applied to the hydrogen issuing from the fine jet,[1] after all atmospheric air has been expelled, *the flame will appear bluish-green* owing to the antimony which is liberated in the decomposition of the hydrogen antimonide, and burns in the flame ; this produces *a white smoke of antimony trioxide*, which is readily deposited on a cold surface, and is not dissolved by water. But if a cold substance, *preferably a porcelain dish, is held in the flame, metallic antimony in an extremely fine state of division is deposited upon it as a deep black, almost lustreless spot.* On heating to redness the middle of the glass tube through which the gas is passing the bluish-green colour of the flame

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[1] The colour of the flame appears particularly distinct and pure when the gas issues from a platinum jet.

diminishes, and, at the same time, a *silvery lustrous metallic mirror of antimony* is produced on both sides of the heated part of the glass tube.

Since compounds of arsenic produce similar stains or a mirror under the same conditions (*cf.* Sec. 89, 12), it is necessary to apply further tests to them, before it can be stated with certainty whether they consist of antimony or contain it. A mirror containing antimony may be identified by the fact that it only volatilises at a fairly high temperature on heating the tube through which hydrogen is still passing, that the hydrogen issuing from the tube has no odour of garlic, that when lighted it only deposits spots upon porcelain when the current of gas is strong, and that the mirror before volatilising melts into small lustrous globules, which are distinctly perceptible with the aid of a lens. With regard to the further differentiation of spots and mirrors of arsenic and antimony, see Sec. 92, 8.

The presence of mercury compounds, especially mercuric chloride, and also of sulphites, has an effect upon the detection of antimony by means of Marsh's apparatus analogous to their effect upon the detection of arsenic (*cf.* Sec. 89, 12).

The behaviour of hydrogen containing hydrogen antimonide towards a solution of silver nitrate or mercuric chloride and towards solid potassium hydroxide will be described in Sec. 92, 9.

13. *On heating an alkaline solution containing antimony ions* (obtained by the use of excess of potassium or sodium hydroxide solution) with *aluminium, zinc,* or a little *magnesium,* hydrogen will be liberated and *the whole of the antimony precipitated.* Hydrogen antimonide is not liberated in the process. (Distinction from arsenite ion, which, when treated in the same way, yields hydrogen arsenide. Hager, Gatehouse.[1]) The test does not distinguish antimony from arsenate ion. Sec. 92, 9 (*d*).

14. When a mixture of a solid antimony compound with *sodium carbonate* or, better, with *sodium carbonate* and *potassium cyanide,* or with *sodium formate* is exposed to the **inner blowpipe flame** in a hollow on charcoal, *round brittle particles of metallic antimony* are obtained, and may be readily identified by the characteristic phenomena which they show on oxidation. For example, if metallic antimony is heated on charcoal before the blowpipe, it produces a *dense white smoke of antimony trioxide,* which forms a deposit on the charcoal; this phenomenon *continues for some time* after

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[1] For a further reaction of antimony, depending on its reduction to metal, see Sec. 89, 16, footnote.

the substance has been withdrawn from the flame; it is especially pronounced when a current of air is directed on to the substance by means of the blowpipe. If, however, the air is checked, so that the smoke rises vertically, the metallic granule will be surrounded by a network of pointed, lustrous crystals of antimony oxide.

15. On introducing antimony compounds into the *upper reducing area of the gas flame* (p. 82), a *greenish-fawn colour* is imparted to the flame, but no odour is diffused; the reduced deposit is black, and either dull or lustrous, whilst the oxide deposit is white. When it is moistened with absolutely neutral silver nitrate solution, and ammonia vapour blown on to it, it gives a black stain (Bunsen)

16. With regard to the *microchemical detection* of the ions of antimony, see Haushofer, *Mikroskopische Reaktionen*, p. 11, Behrens-Kley, *Mikrochemische Analyse*, 3rd ed, p 101; Denigès, *Zeitsch. anal. Chem*, **46**, 601 and 602; Schoorl, *Ibid*, **47**, 375, 381, Sjollema, *Chem. Zentr*, 1908, 1., 762.

SEC. 92.

Summary and Remarks on Group VI., Div 2.

For the detection of the elements of the second division of the sixth group in mixtures or solutions which contain all or several of them, widely varying methods may be employed; and it cannot be stated directly which method is the best, since the choice of one or another method will depend largely upon the proportions in which the substances are present, and upon whether it is desired to attain as high a degree of accuracy as possible, or to accomplish the end in view rapidly without attempting to reach the highest degree of accuracy.

In the following paragraphs we first describe the different methods which are suitable for the separation of *tin*, *antimony*, and *arsenic* from one another,[1] and then the methods of *distinguishing between the different stages of valency of each individual element, and also for the separation of the ions of gold and platinum from those of tin, antimony and arsenic.*

1. If 1 part of a dry mixture of the sulphides of tin, antimony and arsenic is triturated with 1 part of anhydrous sodium carbonat and 1 part of potassium nitrate, and this mixture is introduced littl

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[1] It is obviously impossible to mention here all the different methods proposed, since the reactions, by means of which the three elements may be distinguished, can be grouped together in widely different forms.

by little into a small porcelain crucible, in which 2 parts of sodium nitrate are being fused at not too high a temperature, the sulphides will be oxidised with slight explosion. The fused mass will contain stannic oxide and the arsenate and antimonate of sodium, together with sulphate, carbonate, nitrate, and nitrite. The heat must not be increased to such an extent or continued so long that sodium oxide is formed from the sodium nitrite, since otherwise sodium stannate, which is soluble in water, will be produced. On treating the mass with a little cold water, stannic oxide and disodium dihydrogen pyroantimonate will remain undissolved, whilst sodium arsenate and the rest of the salts will be dissolved. If the filtrate is acidified with nitric acid and heated,[1] so as to expel carbon dioxide and nitrogen trioxide (nitrous anhydride), the arsenate may be separated and identified by means of silver nitrate, as in Sec. 90, 5, or by means of magnesia mixture (Sec 90, 9), or as ammonium arsenomolybdate. On treating the residue of stannic oxide and disodium dihydrogen pyroantimonate (previously washed once with cold water and at least three times with dilute alcohol [2]) with a little hydrochloric acid in the inverted lid of a platinum crucible, and gently heating it, it either dissolves completely, or, if much stannic oxide is present, remains as an insoluble white precipitate. If this is ignored and a fragment of zinc is added, the metals are separated; the presence of antimony is indicated by the blackening of the platinum On then removing the zinc after the evolution of hydrogen has nearly stopped, separating the zinc chloride solution by careful decantation, and heating the contents of the lid with a little hydrochloric acid, the tin will dissolve as stannous chloride, whilst the antimony, if present in considerable quantity, will remain undissolved in the form of black flakes. The former may be identified in the solution by means of mercuric chloride or a mixture of ferric chloride and potassium ferricyanide, and the latter by dissolving it in nitric acid containing a little tartaric acid, and testing the solution with hydrogen sulphide. Should antimony not have been detected with certainty by the foregoing reactions, a portion of the solution obtained by treating the metals with hydrochloric acid is evaporated to a small residue, and, after the addition of a drop of hydrochloric acid, tested on a platinum crucible lid with tin (Sec. 91, 9). Since this method of detecting arsenic, antimony, and tin in the presence of each other is dealt with in the scheme of analysis, we have only described the principles here, and for the details of their application reference must be made to the first chapter of the second part (Rubric No. 120 *et seq.*).

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[1] If a precipitate is formed on acidifying the liquid with nitric acid, it is due to stannic hydroxide, which has separated from the sodium stannate (if the fusion has been made at too high a temperature). Stannic arsenate will also be precipitated with it, so that small quantities of arsenic may be completely precipitated and escape detection.

[2] The removal of arsenate ion is *also* necessary to prevent any hydrogen arsenide being formed in the subsequent treatment. The precipitate must therefore be thoroughly washed. Alcohol is added to prevent the disodium dihydrogen pyroantimonate dissolving.

2. On gently heating a mixture of the sulphides of arsenic, antimony, and tin with fuming hydrochloric acid (after it has been freed from the greater portion of the adherent water by placing the filter containing it on porous paper), the sulphides of tin and antimony dissolve, whilst the arsenic sulphide remains undissolved. The liquid is heated until the hydrogen sulphide has escaped, and is then diluted with a little water, and filtered. If the arsenic sulphide (including the filter paper, if only a very small amount is present) is treated with hot concentrated hydrochloric acid, and the solution diluted with a little water and filtered, the resulting arsenate ion may easily be detected in the filtrate by means of ammonium molybdate (Sec. 90, 9). On treating arsenic sulphide with ammonia solution and evaporating the solution after the addition of a granule of sodium carbonate, an arsenic mirror may be obtained by heating the residue with potassium cyanide and sodium carbonate in a current of carbon dioxide (Sec. 89, 17). The hydrochloric acid solution containing the tin and antimony is heated for a short time with a small bright iron rod and allowed to stand for ten to fifteen minutes. This causes the antimony to separate in black flakes whilst the stannic ion is reduced to stannous ion. The liquid is filtered, and the filtrate tested for stannous ion by means of mercuric chloride. As a confirmatory test the separated antimony may be thoroughly washed and dissolved in nitric acid containing a small quantity of tartaric acid, and the solution treated with hydrogen sulphide.

3. When a mixture of the sulphides is digested with a little ordinary solid ammonium carbonate (mixture of ammonium hydrogen carbonate and ammonium carbamate), $(NH_4HCO_3)NH_4CO_2(NH_2)$ and water at a moderate heat, the arsenic sulphide is dissolved, and may be re-precipitated from the filtrate on acidification, whilst antimony and tin sulphide remain undissolved. This separation however, is not quite complete; traces of the sulphides of antimony and tin are dissolved, whilst a little arsenic sulphide remains in the

residue. It is, therefore, necessary, when absolute certainty is required, to wash the precipitated arsenic sulphide obtained by acidifying the alkaline solution (especially when it consists of only a few flakes) and to treat it with ammonia solution, to evaporate the solution after the addition of a granule of sodium carbonate, and to fuse the residue with potassium cyanide and sodium carbonate in a current of carbon dioxide, so as to obtain an arsenic mirror. The residue, insoluble in ammonium carbonate solution, should be treated as in 2.

4. In the analysis of metal alloys a residue, insoluble in nitric acid and consisting of stannic oxide, oxygen compounds of antimony and arsenic pentoxide is frequently obtained. This is fused (preferably with sodium hydroxide) in a silver crucible,[1] the mass stirred with a little water, the liquid treated with a third of its volume of 86 per cent (by weight) alcohol, and filtered, and the insoluble residue of disodium dihydrogen pyroantimonate washed with dilute alcohol to which a few drops of sodium carbonate solution have been added. In the presence of much tin it is advisable to treat the residue again in the same way, in order to extract the whole of the stannate. The filtrate is acidified with hydrochloric acid and the ions of tin and arsenic precipitated from the hot solution as sulphides, which are then separated, preferably as in 2.

A similar method has been proposed by O. Kassner (*Zeitsch. anal. Chem.*, **34**, 596), in which the moist sulphides are mixed with water and oxidised with sodium peroxide, the liquid evaporated in a silver crucible, and the residue fused. The filtrate from the insoluble disodium dihydrogen pyroantimonate is slightly acidified with sulphuric acid, the stannate ion precipitated with ammonium chloride[2] and the arsenate ion precipitated by means of magnesia mixture from the filtrate (*cf.* also Walker, *Zeitsch. anal. Chem.*, **46**, 606). Petersen (*Zeitsch. anorg. Chem.*, **88**, 108; *Zeitsch. anal. Chem.*, **54**, 375) boils the sulphide with 10 to 15 c.c. of water and a spatula full of sodium peroxide. Disodium dihydrogen pyroantimonate separates on cooling the liquid. Stannate ion and arsenate ion may be detected in the filtrate, *e.g.* as in Kassner's method above. For the detection of arsenic Petersen recommends the use of Bettendorf's reaction (Sec. 89, 15), after the addition of concentrated hydrochloric acid to the filtrate. If much tin is present, the solution of the fused mass may be turbid under certain conditions. In that case it should be filtered while hot; the antimonate separates from the filtrate on cooling.

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[1] For the method of using this, see p. 58.

[2] See footnote 1, p. 368.

F. L. Hahn (*Zeitsch. anorg Chem.*, **92**, 168; *Zeitsch. anal. Chem*, **56**, 53) extracts the mixtures of sulphide and sulphur with sodium sulphide solution in the cold, adds about twice the volume of 10 per cent. sodium hydroxide solution and hydrogen peroxide, and heats the liquid if necessary to boiling point. The evolution of oxygen shows that enough hydrogen peroxide is present. The addition of alcohol soon causes the precipitation of disodium dihydrogen pyroantimonate to be complete. Hahn's method of separating stannate and arsenate ions in the filtrate is essentially the same as that of Kassner, since after evaporating the alcohol he adds ammonium nitrate[1] and expels the ammonia by boiling.

5. If, therefore, it is a question of detecting very small quantities of arsenic ions in the presence of large amounts of tin and antimony ions, it is advisable to distil the solution containing the chlorides with not too small a quantity of fuming hydrochloric acid and ferrous chloride or ferrous sulphate,[2] using a receiver containing chilled water, until about a fourth of the liquid has distilled, and to test the distillate with hydrogen sulphide (E. Fischer, F. Hufschmidt, A. Classen). The method is less suitable for the simultaneous detection of antimony and tin ions, since the distillation must then be continued and repeated until the whole of the arsenic ion has distilled, in which case small quantities of antimony and tin ions may also be found in the distillate; and also on account of the fact that in precipitating tin and antimony by means of hydrogen sulphide from the distillation residue the sulphides are obtained in admixture with a large amount of sulphur. A solution suitable for distillation can only be obtained from the sulphides by heating them with hydrochloric acid, with the addition of a little potassium chlorate, or more conveniently by suspending them in water and introducing sodium peroxide (Th. Poleck), or by heating them with concentrated sulphuric acid (Plato).[3]

Arsenic may be separated from alloys in a similar manner by distillation of a hydrochloric acid solution with a large amount of ferric chloride. Under these conditions during the solution of the alloy, reduction to ferric chloride takes place with little, if any, evolution of hydrogen, so that only arsenic trichloride distils (L. de Koninck, *Chem. Zentr.*, 1895, II, 1132).

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[1] If tin is precipitated by means of ammonium chloride or nitrate, arsenic may be present in the tin precipitate.

[2] Before using the reagents mentioned for the detection of small quantities of arsenic, it is necessary to test them by the distillation method, to be certain that they themselves are absolutely free from arsenic.

[3] For details of a distillation method of separating the three elements, which, however, is more suitable for quantitative purposes, see Plato (*Zeitsch. anorg. Chem.*, **68**, 26; *Zeitsch. anal. Chem.*, **50**, 641; W. Hartmann (*Ibid.*, **58**, 148).

Arsenic and antimony ions may be separated from each other by treating them with methyl alcohol and hydrochloric acid, and distilling the liquid at the temperature of the water bath. Only arsenic trichloride distils, whilst antimony ions remain in the residue (Friedheim and Michaelis, *Zeitsch. anal. Chem.*, **39**, 708; Cantoni and Chautems, *Ibid.*, **49**, 720; Moser and Perjatel, *Ibid.*, **52**, 314; Collins, *Ibid.*, **52**, 594). The last-mentioned chemist points out that, to prevent the possibility of simultaneous distillation of antimony ions, all moisture must be excluded.

6. Arsenic and antimony ions may be readily separated by treating 1 part of the solution with 2 parts or more of hydrochloric acid of sp. gr 1·2, and introducing hydrogen sulphide gas. The arsenic ion is then precipitated, either as trisulphide or pentasulphide, according to the conditions, whilst antimony ion remains in solution, but may be precipitated with hydrogen sulphide after diluting the liquid with water (O Kohler, Neher). A similar method may be used for the separation of antimony ion from tin ion, the solution containing the tin in tetravalent form being treated with concentrated hydrochloric acid of sp. gr 1·18, and diluted in such a way that for each part of water 1 part of this acid is present, since from such a solution only the antimony ions and not the tin ions are precipitated by gaseous hydrogen sulphide (Loviton). According to Le Roy W McCay, and also K Thiele, the separation of stannic and antimonous ions may also be effected by treating the hydrochloric or sulphuric acid solution with hydrofluoric acid, only antimony sulphide being then precipitated from this solution by means of hydrogen sulphide (*Zeitsch. anal. Chem.*, **51**, 680)

If successive precipitation with hydrogen sulphide is to be used for the separation of the three elements, arsenic (which should preferably be in the trivalent condition) and antimony ion are first precipitated together from a hot solution containing much oxalic acid these sulphides dissolved (as described in No. 5 at the end of the first paragraph) and then separated from a solution in strong hydrochloric acid by the method outlined above. The tin ion may be precipitated from the first solution by means of hydrogen sulphide, after decomposition of the oxalic acid by means of potassium permanganate, or it may also be separated as tin sulphide by treating the solution with ammonia and ammonium sulphide and then adding acetic acid.

7. On adding a saturated aqueous solution of hydrogen sulphide to a solution containing pentavalent arsenic and antimony ions (which has been acidified with hydrochloric acid), and then passing a current of air through the liquid for a few minutes in order to remove the excess of hydrogen sulphide, the precipitate will contain the whole of the antimony as pentasulphide, but no arsenic. The latter may subsequently be precipitated by heating the filtrate to 70°, and introducing a current of hydrogen sulphide (Bunsen).

8. In Sec. 89, 12, and Sec. 91, 12, it is stated that in Marsh's test spots and a mirror may be produced both by arsenic and antimony. To differentiate them it may be noted that the spots deposited from a flame upon a cold surface by arsenic are brownish-black and more lustrous, whilst those produced by antimony are dull and deep black. Arsenic stains may also be readily distinguished from antimony stains by treating them with a freshly prepared solution of sodium hypochlorite[1] and sodium chloride (made by adding sodium carbonate to a solution of chloride of lime, and filtering the liquid), in which arsenic stains dissolve immediately, whilst antimony stains are insoluble or only dissolve after a considerable time.[2] Another method of identifying arsenic stains is to heat them with a few drops of concentrated hydrochloric acid. They dissolve as arsenic acid, which may be readily detected by means of ammonium molybdate (see Sec. 90, 9 (Denigès)).

The methods described in Sec. 91, 12, and 89, 12, are quite sufficient for distinguishing between an arsenic mirror and an antimony deposit, but in many cases will not permit of the certain detection of arsenic when present in admixture with antimony. The best method of arriving at a certain conclusion in such cases is as follows:—

The long tube, through which is passed the gas to be subjected to further tests, is heated to redness in several places, so as to obtain as pronounced a metallic mirror as possible. A very weak current of dry hydrogen sulphide is then passed through the tube, and the metallic mirror heated by means of a Bunsen burner, starting from its outer edges. In this way, when only arsenic is present, yellow arsenic sulphide is formed in the tube, whilst when only antimony is present, orange or black antimony sulphide is obtained, but if the metallic mirror consisted of arsenic and antimony, both sulphides are produced, but in such a way that arsenic sulphide, as the more volatile, is invariably formed before the less volatile antimony sulphide. On now passing dry hydrogen chloride through the tube, which contains arsenic sulphide, antimony sulphide, or both, but without applying heat, no change will be observed if only arsenic sulphide is present, even when the gas has passed over the sulphide for a long time. If only antimony is present, everything will be volatilised from the tube, and if the current of gas is conducted into water, antimony chloride may be readily detected in the latter by means of hydrogen sulphide. Lastly, if both arsenic and antimony are present, the antimony sulphide soon volatilises, leaving the yellow arsenic sulphide behind. On introducing a little ammonia solution into the tube, the arsenic sulphide will be dissolved and so may easily be distinguished from separated sulphur. These various reactions when used in combination never fail, according to the experiments of R. Fresenius, to detect the presence of arsenic. The following method for distinguishing between the deposits also depends upon the same chemical processes. The deposit is obtained on a glass plate and moistened with ammonium sulphide solution, which is then evaporated with the aid of heat, and the glass placed, with the deposit downwards, over a beaker containing fuming hydrochloric acid. If only antimony is present the orange coloured residue will disappear, whilst in the presence of arsenic yellow arsenic sulphide will be left (J. T. Anderson).

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[1] According to Vaubel and Knoeke (*Zeitsch. anal. Chem.*, **55**, 512) antimony stains are soluble in hypochlorite solution which has been kept for some time.

[2] Bismuth stains, which may be obtained when bismuth preparations are tested directly in Marsh's apparatus, are insoluble in sodium hyposulphite solution (B. P. Cladwell, *Zeitsch. anal. Chem.*, **48**, 654).

9. Antimony and arsenic may also be separated by the following methods, when present in the form of a mixture of their hydrogen compounds: (*a*) The gases, mixed with excess of hydrogen, are passed through a rather wide glass tube containing pieces of potassium hydroxide for a layer of at least 10 cm. The potassium hydroxide decomposes the hydrogen antimonide, and consequently the glass becomes coated with a lustrous metallic film, whereas the hydrogen arsenide remains practically undecomposed, and may, therefore, be easily detected in the gas (free from antimony), which leaves the tube, by the formation of spots or rings (Sec. 89, 12), or by its action on a solution of silver nitrate (Dragendorff). (*b*) The gas, mixed with excess of hydrogen, is passed through a tube containing fragments of glass moistened with dilute lead acetate solution to remove hydrogen chloride and hydrogen sulphide, and is then conducted

in a slow current into a solution of silver nitrate. The antimony contained in the gas is precipitated almost completely as black silver antimonide, Ag_3Sb, whilst the arsenic causes reduction of the silver, is dissolved as arsenious acid, and may be detected in the solution as silver arsenite by the careful addition of ammonia solution, or by means of hydrogen sulphide after precipitation of the excess of silver ion with hydrochloric acid. But since some antimony is invariably dissolved, the precipitate, produced in the solution by means of hydrogen sulphide, must not be regarded as arsenic sulphide without a confirmatory test. This test may be made as described in Sec. 92, 2. The antimony is most readily detected in the precipitated silver antimonide (which is often mixed with much silver) by boiling the precipitate with water until arsenious acid and silver nitrate are completely removed, and then heating it to boiling point with tartaric acid and water. Only the antimony then dissolves, and may easily be detected by means of hydrogen sulphide in the solution after acidification with hydrochloric acid (Lassaigne, A. W. Hofmann). (*c*) A slowly evolved current of the gas is conducted through a mixture of 2 c c. of silver nitrate solution (1 part of silver nitrate, 24 parts of water), 2 c c. of concentrated nitric acid, and 8 to 10 c.c. of water. When the resulting black precipitate subsides in the liquid the reaction may be regarded as complete. An excess of bromine water is then introduced into the small flask containing both liquid and precipitate, or hydrochloric acid is added, together with so much potassium chlorate that a large excess of chlorine is present, and the liquid filtered after some time. The filtrate is treated with tartaric acid, ammonium chloride, and excess of ammonia solution, the arsenic (now present as arsenate ion) precipitated as ammonium magnesium arsenate (Sec. 90, 8), and filtered off after standing for some time, the filtrate acidified with hydrochloric acid, and the antimony ion precipitated with hydrogen sulphide (E. Reichardt). (If the liquid, brought into contact with zinc and sulphuric acid in the methods (*a*), (*b*), or (*c*), also contained tin ion, this will be separated in metallic form by the continuous action of the zinc. If, therefore, the zinc solution is decanted, the residue heated with hydrochloric acid, the solution filtered and the filtrate treated with mercuric chloride solution, the presence of tin ion is indicated by the formation of a precipitate of mercurous chloride). (*d*) When a solution containing trivalent (but not pentavalent) arsenic ion is introduced into an apparatus in which hydrogen is evolved from an alkaline solution (*e.g.* one containing potassium hydroxide solution and arsenic-free aluminium foil or wire), and the gas is conducted through silver nitrate solution, a blackening of the liquid is distinctive of arsenic, since hydrogen antimonide cannot be formed under these conditions. (*e*) When hydrogen arsenide or antimonide is brought into contact with pure filter paper which has been moistened with a solution of silver nitrate, the moistened parts of the paper are coloured. If, as directed by Gutzeit, a solution containing 1 part of silver nitrate in 1 part of water is used, hydrogen arsenide produces a lemon-yellow stain, which becomes black when a drop of water is applied, whilst hydrogen antimonide produces a dark brownish-red to black stain at the edges of the place which has been moistened with silver nitrate solution. The inner portion either shows no coloration or, at most, a pale grey one. Paper moistened with dilute (*e.g.* 1 : 4) silver nitrate solution is stained black by both gases. These reactions (in using which it is necessary to bear in mind that hydrogen sulphide and phosphide produce similar colorations) have been used in various modifications and subjected to different criticisms; for example, Ritsert recommends the use of an ammoniacal solution of silver nitrate. Paper moistened with such a solution becomes dull brown to black on contact with the slightest trace of hydrogen arsenide. The reaction is not affected by steam or acid vapours, or by the action of the paper, but the presence of hydrogen sulphide or phosphide interferes with it, as does also hydrogen antimonide, which last also produces brown or black stains. A complete summary and critical examination of these methods has been made by H. Beckurts,[1] to which reference may be made. (*f*) On moistening pure filter paper with a drop of a saturated alcoholic solution of mercuric chloride, allowing the liquid to evaporate, repeating this treatment four or five times, and bringing the paper thus prepared into contact with hydrogen arsenide, a pale yellow stain, changing to orange on continuing the action of the gas, is obtained. Hydrogen antimonide, when present in minute quantity, has no effect, but in larger amounts produces a brown to greyish-black stain. If the stain has been derived from both hydrogen compounds, it is possible, if not too much hydrogen antimonide has acted on the paper, to detect that produced by hydrogen arsenide by cutting the spot out of the paper and moistening it on a clock-glass with a drop of 74 per cent. (by weight) alcohol. The colour produced by hydrogen antimonide will disappear after standing for some time, and allow the yellow coloration produced by hydrogen arsenide to be recognised (Flückiger, Lohmann [1]). (*g*) A combination of methods (*e*) and (*f*) is recommended by P. H. Conradson (*Zeitsch. anal. Chem.*, **39**, 655). He uses filter paper, impregnated with (1) lead acetate, (2) silver nitrate, (3) filter paper saturated with mercuric chloride, and (4) filter paper upon which two drops of nitric acid of sp. gr. 1·2 have been placed and two drops of potassium iodide solution introduced into the middle of the nitric acid stain. Hydrogen is evolved in the manner described in Sec. 89, 12, tested for purity by means of papers 1 and 2, and the substance under examination added. After the absence of hydrogen sulphide has been proved by means of 1, the paper 2 is used for testing whether arsenic or antimony ions are present. If a positive reaction is obtained, the test paper 3 will give a lemon-yellow stain, gradually becoming yellowish-brown in the presence of arsenic. Antimony gives a grey-brown stain without any yellowish tone. If a stain of this colour *without* yellow edges is obtained immediately, it may be considered a proof of the absence of arsenic ion. If antimony ion has not been detected in this last test, a further test is made with paper 4, which, in the presence of antimony, becomes yellow to orange-red in colour.

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[1] *Pharm. Zentralhalle*, **25**, 197, 209, 223; *cf.* also Gotthelf, *Zeitsch. anal. Chem.*, **44**, 258; Strauss, *Ibid.*, **45**, 666; Kirkby, *Ibid.*, **46**, 477.

10. Finally, the attention of chemists who are expert in flame tests may be directed to the method of Bunsen (*Zeitsch. anal. Chem* 5, 378), which enables all three elements to be identified in the precipitate of the sulphides by means of flame reactions and blowpipe tests.

11. *Stannous and stannic compounds* may be detected in the presence of each other by testing one portion of the solution (containing both substances) for stannous ion by means of mercuric chloride, auric chloride, or a mixture of potassium ferricyanide and ferric chloride, and a second portion (which must contain very little free acid) for stannic ion by pouring it into a boiling solution of sodium sulphate.

12. *Trivalent antimony ion* may be detected in the presence of *pentavalent antimony* by means of the reaction given in Sec. 91, 11. *Pentavalent antimony* may be detected in the presence of trivalent antimony by treating the oxide, which must be free from other substances, with hydrochloric acid and potassium iodide (Sec. 91,

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[1] *Cf.* Dowzard, *Zeitsch. anal. Chem.*, **43**, 415; Perkin and Goode, *Ibid.*, **50**, 598.

2 and 3), or by treating the solution with sulphuric acid, cooling it, and adding a drop of a solution of diphenylamine in concentrated sulphuric acid, whereby in the presence of antimonate ion the liquid assumes a deep blue colour. This reaction, however, is only distinctive of antimonate ion, when the ions of other substances which give a similar coloration with diphenylamine, such as nitric acid, chromic acid, etc., are not present.

13. Arsenite and arsenate ions may be distinguished from each other in a solution by means of silver nitrate. If the precipitate contains silver arsenate and much silver arsenite, the former can only be detected by adding extremely dilute nitric acid drop by drop, whereby the yellow silver arsenite is dissolved first. For the detection of even fairly small quantities of arsenate ion in the presence of arsenite ion, magnesia mixture (Sec. 90, 8 [1]) is also a suitable reagent. Trivalent arsenic may also be detected in the presence of pentavalent antimony by the fact that in a moderate solution it gives a precipitate at once with hydrogen sulphide with the aid of heat, which is not the case with pentavalent arsenic, as also by the fact that only trivalent arsenic forms hydrogen arsenide, when introduced into a solution of sodium hydroxide acting upon aluminium. It may also be easily detected by the reduction effected in an alkaline solution of a cupric salt by trivalent arsenic, as well as by the fact that on boiling an ammoniacal solution of a silver salt in presence of arsenite ion metallic silver is precipitated.

If the degree of sulphonation of the arsenic in a sulpho salt is to be determined, the alkaline solution (from which any sulphur present has been extracted by means of carbon bisulphide) is boiled with bismuth hydroxide and filtered from the bismuth sulphide, and tests for arsenite and arsenate ion applied to the filtrate. Arsenic trisulphide may be distinguished from arsenic pentasulphide by first completely extracting any sulphur present by means of carbon bisulphide, dissolving the residue in ammonia solution, immediately adding an excess of silver nitrate solution, filtering off the silver sulphide, and noting whether silver arsenite or arsenate is produced on adding nitric acid to the filtrate. In the case of these last tests, however, it should be noted that some of the arsenic may be found in the bismuth sulphide as well as in the silver sulphide (Waitz).

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[1] According to our experience the objections which Lutz and Swinne (*Zeitsch. anorg. Chem.*, **64**, 298) and Brunnich and Smith (*Ibid.*, **68**, 292) have brought against these methods of detecting arsenate ion in the presence of arsenite ion are only applicable to cases where a precipitate is first formed after several hours, since arsenite ion under such conditions also gives a very small crystalline precipitate. In all cases in ordinary qualitative analysis the methods may be regarded, as heretofore, as absolutely trustworthy.

14. *Gold* and *platinum ions* may be separated from *tin* and *antimony ions* (apart from the method of heating the sulphide in a current of chlorine, as described in the systematic course, or in a current of air after admixture with ammonium nitrate), by boiling the solution with excess of sodium hydroxide solution and chloral hydrate. The resulting precipitate contains the whole of the gold and platinum and is free from the other metals.

Gold and platinum may also be precipitated by means of sodium hydroxide and a hydrazine salt, whilst arsenic, antimony, and tin ion remain in solution. The solution under examination (containing about 1 grm. of substance) is poured into a mixture of 40 c.c. of 20 per cent. sodium hydroxide solution and 20 c.c. of a cold saturated solution of hydrazine sulphate (or 5 c.c. of hydrazine chloride solution 1 : 5), the liquid slowly heated to boiling point, diluted with twice its volume of water, cooled, and filtered (Knoevenagel and Ebler, *Ber.*, **35**, 3055).

SPECIAL REACTIONS OF THE RARER MEMBERS OF THE SIXTH GROUP.

SEC. 93.

1. Iridium, Ir, 193·1.

Iridium, which is associated with the members of the sixth group of more frequent occurrence—the noble metals[1]— is *divalent*, *trivalent*, and *tetravalent*. The compounds of the divalent ion are very unstable. Iridium has a slight tendency to form cations; on the other hand, it combines with chlorine to form complex anions, $IrCl'''_6$ and $IrCl''_6$. Iridium occurs in combination with platinum and other metals in platinum ores, especially as osmium-iridium. It has of recent years been used in alloy with platinum for crucibles, etc.

1. Iridium is a metal resembling platinum, but is brittle; it is extremely difficult to melt (melting point 2200°), and has a specific gravity of 22·4. In the compact form, or when reduced by hydrogen at a red heat, it is not soluble in any acid, even *aqua regia*. (Distinction from gold and platinum.) When reduced by the wet method, however, as for example by means of formic acid, or when alloyed with platinum, it dissolves in *aqua regia*, in the form of ions of iridic chloride (tetrachloride), $IrCl_4$. It is oxidised, but not rendered soluble, by fusion with potassium hydrogen

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[1] With regard to its detection in the presence of other platinum metals, see Sec. 86.

sulphate. (Distinction from rhodium.) When fused with sodium hydroxide in the presence of air, or with sodium nitrate, it is oxidised. The resulting sodium compound - a derivative of iridium sesquioxide, Ir_2O_3—is partly soluble in water. When heated with *aqua regia* it dissolves, forming a blackish-red solution, which contains the ions of sodium iridic chloride, Na_2IrCl_6.

2. On treating a mixture of powdered iridium and *sodium chloride*, heated to incipient redness, with *gaseous chlorine*, *sodium iridic chloride* is formed; this dissolves in water to form a deep reddish-brown solution. (*a*) *Potassium hydroxide* added in excess to this solution changes the colour to a greenish shade, while a little brownish-black *potassium iridic chloride* is simultaneously precipitated. (*b*) On heating the solution and exposing it for some time to the air, it becomes first reddish, then violet, and finally blue, owing to the absorption of oxygen and formation of *iridic hydroxide* (Claus) (Characteristic distinction from platinum ion.) (*c*) On evaporating the solution to dryness and treating the residue with water, an insoluble blue deposit of iridic oxide, IrO_2, is left, whilst the liquid is colourless.

3 On treating with concentrated hydrochloric acid iridic chloride, as obtained by repeatedly evaporating ammonium iridic chloride with *aqua regia*, and finally with hydrochloric acid, a *dark brown solution* is obtained. *Solutions of iridic chloride* behave as follows:—

4. On heating an iridic chloride solution with *sulphuric acid* until acid fumes escape, and treating the residue with boiling water, a clear solution, which is usually green, but sometimes blue or violet, will be obtained. (*a*) If this solution is neutralised with *potassium hydroxide*, and boiled for fifteen to twenty minutes, finally after the addition of potassium hydroxide in excess, an oxide will be precipitated; this is soluble in dilute sulphuric acid, forming a bright violet solution. (*b*) If *ammonium nitrate* is introduced in small portions after fumes of sulphuric acid have ceased to be evolved, when the iridium salt has been heated with that acid, and withdrawn from the flame, there is produced a blue (sometimes emerald-green) mass, which, if the operation is stopped before all the ammonium nitrate has been added, will dissolve in water to form a blue solution. The presence of other platinum metals naturally influences the sensitiveness of the reaction.

5. On heating *iridic chloride* directly with successive quantities of *ammonium nitrate* and *ammonium chloride*, there will be produced, not a blue, but a pink mass, from which a pink powder may be separated by treatment with a very little water (Lecoq de Boisbaudran).

6. *Hydrogen sulphide* at first produces an olive-green coloration in solutions of iridic chloride, iridous ion, $Ir^{\cdot\cdot\cdot}$, being formed, whilst sulphur separates; subsequently brown *iridous sulphide*, Ir_2S_3, is precipitated.

7. *Ammonium sulphide* precipitates the same compound, which dissolves readily in excess of the precipitant.

8. On treating a solution of iridic chloride with *sodium hydroxide* and *sodium hypochlorite* or *hypobromite*, *blue iridic oxide* will be precipitated.

This is a very characteristic reaction (Mylius and Mazzucchelli, *Zeitsch. anorg. Chem.*, **89**, 14. *Vide supra* 2 (*b*) and (*c*)).[1]

9. *Potassium chloride* precipitates *potassium iridic chloride*, K_2IrCl_6, as a crystalline blackish-red powder, which is insoluble in a concentrated solution of potassium chloride.

10. *Ammonium chloride* precipitates *ammonium iridic chloride* from concentrated solutions in the form of a blackish-red powder, consisting of microscopic octahedra, insoluble in concentrated ammonium chloride solution. In the presence of platinum ion the precipitate is red. This may easily cause confusion with palladium, rhodium, ruthenium, and osmium ions (Mylius and Mazzucchelli, *loc. cit.*).

11. Ammonium or potassium iridic chloride becomes olive-green, especially in hot solution, on the addition of *potassium nitrite*, while *ammonium* or *potassium iridous chloride* is formed: $IrCl''_6 + NO'_2 = IrCl'''_6 + NO_2$; for example, $K_2IrCl_6 + KNO_2 = K_3IrCl_6 + NO_2$; on cooling the liquid the double salt crystallises. When the green solution is *heated or evaporated with an excess of potassium nitrite* it becomes yellow, and on then boiling the liquid a *white compound*, very sparingly soluble in water and hydrochloric acid, is precipitated. (Essential distinction and method of separation from platinum ion. Gibbs.)

12. On dissolving *ammonium iridic chloride* by boiling it with water, and adding *oxalic acid*, *reduction* to *ammonium iridous chloride* takes place, so that the solution remains clear when cooled. (Distinction from platinum ion. C. Lea.)

13. On boiling a solution of iridic chloride with *stannous chloride*, adding excess of *potassium hydroxide*, and heating the liquid, a *leather-coloured precipitate* is obtained.

14. *Ferrous sulphate*, *oxalic acid*, *sulphur dioxide*, *hydrogen peroxide*, and *alkali* [2] or *hydroxylamine*,[3] do not precipitate iridium from a solution of iridic chloride. (Method of separating iridium ion from gold ion.)

15. *Zinc* precipitates *black iridium*.

16. According to Quennessen, *magnesium* also produces a precipitate (probably an oxide), which becomes blue at 100°. It dissolves in sulphuric acid and also in acetic acid to form solutions, the colour of which varies according to the temperature to which the precipitate was heated (*Bull. Soc. Chim.*, (3), **33**, 875; *Chem. Zentr.*, 1905, II., 854).

17. *Acetylene* does not precipitate iridium from solutions of its salts. (Distinction from palladium ion. Makowka, *Zeitsch. anal. Chem.*, **46**, 117.)

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[1] In the case of solutions of platinum salts, the best method of applying the test is to make the solution very dilute, to add sodium carbonate until it is slightly alkaline, to heat it to 100°, and, after cooling, to treat it with a very little slightly alkaline sodium hypobromite solution. If much platinum is present, the liquid must be heated to cause the iridic oxide to separate. Pure dilute platinum chloride solution does not give a precipitate, although the blue precipitate invariably contains platinum; if the latter was present with iridium all other heavy metals, except gold, will be simultaneously precipitated.

[2] Vanino and Seeman, *Ber.*, **32**, 1968.

[3] Jannasch and Mayer, *Ibid.*, **38**, 2130.

18. If iridium oxide is suspended in a solution of *potassium sulphite*, the liquid saturated with *sulphur dioxide*, and then boiled until all free sulphur dioxide has been expelled, the evaporated water being meanwhile renewed, the whole of the iridium oxide will be converted into insoluble iridium sulphite (whilst any platinum oxide present will remain in solution as potassium platinosulphite). (C. Birnbaum.)

19. When *ignited* with *sodium carbonate*, iridium compounds yield in the *upper oxidising flame* a deposit of metal, which, when triturated, is grey, non-lustrous, and not malleable.

20. When a partly dehydrated *borax bead* is moistened with a dilute iridium solution and again fused to a clear bead, the latter appears *light-brown*, but, in contradistinction to platinum, does not appear turbid by reflected light.

21. Iridium compounds show the "*ignition reaction*" (*cf.* Sec. 85, 14).

22. With regard to the *microchemical detection* of iridium, see Behrens Kley, *Mikrochemische Analyse*, 3rd ed., p. 165.

SEC. 94.

2. Germanium, Ge, 72·5.

1. *Germanium* is *divalent* and *tetravalent*. Hitherto it has only been found in small quantity in argyrodite and euxenite, and in niobium and tantalum minerals (*e.g.* samarskite, fergusonite, niobite, gadolinite). It combines with oxygen to form two oxides, the monoxide (*germanous oxide*), GeO, and the dioxide (*germanic oxide*), GeO_2. On reducing its oxides in a current of hydrogen, it is obtained as a powder, which can be fused with borax into a greyish-white lustrous metallic button. This has a specific gravity of 5·469, is easily friable, and does not alter in the air. It melts at about 900°. Germanium volatilises at a bright red heat, and forms a sublimate consisting of small crystals. It does not dissolve in hydrochloric acid, but is converted by nitric acid into white germanic oxide, and by hot concentrated sulphuric acid into a white sulphate, soluble in water, while sulphur dioxide is evolved. The metal is readily soluble as chloride in *aqua regia*. Concentrated potassium hydroxide solution does not dissolve it, but on fusion with potassium hydroxide it yields potassium germanite, the reaction being of an explosive character. In its general chemical behaviour germanium forms a transition stage between silicon and tin, which is also in accordance with its position in the periodic system.

2. *Germanic oxide* is formed by the combustion of the metal in oxygen, by the spontaneous oxidation of germanium sulphide, by treatment of the metal with nitric acid, decomposition of the chloride by means of water, etc. It is a compact, white powder, dissolving with difficulty in water, and showing a considerable tendency to be converted into the colloidal condition. It can be heated to bright redness without undergoing alteration. Its aqueous solution has an acid reaction, and therefore

presumably contains anions with the formula GeO''_3. Germanic oxide dissolves *readily* in alkali hydroxide solutions; it also dissolves, though with difficulty, in acids, cations $Ge^{\cdot\cdot\cdot\cdot}$ being formed. When fused with alkali hydroxides and carbonates, it is converted into water-soluble compounds.

3. *Germanic chloride*, $GeCl_4$, is obtained by heating the metal or its sulphide in a current of chlorine. It is a thin colourless liquid, which boils at 86°, and is volatile even at the ordinary temperature; it is decomposed by water with the formation of oxide, which is partly precipitated. On acidifying an aqueous solution of the chloride with hydrochloric acid and evaporating the liquid to dryness, the chloride is completely volatilised (C. Winkler).

4. *Hydrogen sulphide* produces a voluminous white precipitate of *germanic sulphide*, GeS_2, in acid solutions of the salts of tetravalent germanium; the precipitation is only complete in the presence of a considerable excess of a strong acid. Germanic sulphide is somewhat soluble in water, and in hydrogen sulphide water, so that it cannot be washed with the latter. Hence, to obtain it in pure condition, it must be washed first with hydrochloric acid or sulphuric acid saturated with hydrogen sulphide, then with alcohol saturated with hydrogen sulphide, and finally with ether. When dried it is a soft white powder. On heating it in a current of carbon dioxide, a characteristic odour recalling that of acrolein is produced, while the sulphide becomes yellow or greyish-yellow and diminishes in quantity. When heated to bright redness it volatilises. *Germanic sulphide* is *readily soluble* in *ammonium sulphide solution*, forming salts of a very stable sulpho acid. On adding a sufficient *excess of acid*, it is precipitated (unchanged) from this solution as a *white precipitate*. (This is a characteristic reaction.) When it separates in admixture with sulphur it may easily be distinguished from the latter by the fact that it dissolves on washing the precipitate with water. It may be separated from sulphur by treatment with ammonia solution, whereby only the germanic sulphide is dissolved. On then acidifying this solution, it separates as a characteristic voluminous precipitate. If arsenic sulphide or antimony sulphide is also present, either of these may first be precipitated from the ammoniacal solution by adding acid drop by drop. The liquid is then filtered, and white germanic sulphide precipitated by adding an excess of acid to the filtrate.[1] Germanic sulphide is also readily soluble in potassium hydroxide or ammonia solution. It is dissolved by *aqua regia*, with the separation of sulphur. Nitric acid converts it into a mixture of an oxide containing sulphuric acid and sulphur. When germanic sulphide is heated in a current of hydrogen, brownish-red

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[1] For the separation of germanium from antimony and tin, the sulphide precipitate may be treated with ammonium carbonate solution, which dissolves only the germanic sulphide. It may be separated from arsenic sulphide, which dissolves with the germanic sulphide, by distilling the hydrochloric acid solution in a current of chlorine or after the addition of potassium chlorate or permanganate (Buchanan, *Chem. Zentr.*, 1918, I., 73). For the complete separation of arsenic the distillation temperature must be raised to over 108° (up to 116°) (P. E. Browning and S. E. Scott, *Chem. Zentr.*, 1918, I., 948).

germanous sulphide, GeS, is formed, while hydrogen sulphide is liberated. On continuing the heating the germanous sulphide is partly reduced to germanium.

5. *Zinc* slowly precipitates the metal from solutions of germanium salts in the form of a dark brown pasty deposit.

6. When heated on charcoal in the reducing flame of the *blowpipe* without the addition of alkali, germanium oxide yields a metallic button, with the simultaneous formation of a white deposit of oxide.

7. *Borax* and *alkali phosphate* dissolve germanium compounds readily both in the oxidising and reducing flame, to form beads which are colourless, both while hot and cold, and are not changed when heated with tin.

8. *Non-luminous flames* are *not* coloured by germanium compounds.

9. Small quantities of germanium in argyrite may easily be detected by heating the mineral in an atmosphere of hydrogen sulphide or of coal gas. In this way a sublimate resembling antimony sulphide is obtained; this shows very characteristic forms under the microscope, and may be subjected to further tests by the wet method (Haushofer [1]).

SEC. 95.

3. Selenium, Se, 79·2.

1. *Selenium* is *divalent*, *tetravalent*, and *hexavalent*. It is of rare occurrence in nature in the form of metallic selenides, but is frequently present in small quantities in numerous pyrites, and is, therefore, also found in sulphuric and hydrochloric acids. In accordance with its position in the periodic system, selenium closely resembles sulphur on the one hand and tellurium on the other in its chemical behaviour. Elementary selenium exists in several modifications, the specific gravity of which ranges from 4·27 to 4·8. It melts at 277°. Selenium which has been fused is greyish-black, volatile at higher temperatures, and sublimable; when heated in the air it burns, emitting a *characteristic odour recalling that of decomposing radishes*, and forming selenium dioxide (selenious anhydride), SeO_2. The vitreous modification, α-selenium, dissolves with difficulty, but completely, in carbon bisulphide; the red modification, β-selenium, is still less soluble, and metallic or γ-selenium is hardly, if at all, soluble in that medium. On contact with mercury the solution yields black mercuric selenide, HgSe. Cold concentrated sulphuric acid dissolves selenium, without oxidising it, to form a dark green liquid (a sensitive reaction), from which on dilution the selenium separates in red flakes. When boiled with concentrated sulphuric acid, selenium is oxidised and dissolves as selenious acid; it is also dissolved as selenious acid by nitric acid and by *aqua regia*. When heated in a current of hydrogen, selenium forms gaseous hydrogen selenide, H_2Se, which resembles hydrogen sulphide in its reactions.

2. *Selenium dioxide*, SeO_2, is a solid hygroscopic substance, which is converted at about 200° C. into a dark yellow gas, and yields a white

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[1] *Sitzungber. Munch. Akad.*, 1887, 133; *Chem. Zentr.*, 1888, 867.

sublimate of white quadrilateral needles. *Selenious acid*, H_2SeO_3, forms crystals resembling nitre. Both of these compounds dissolve in water, forming strongly acid liquids.

3. Of the neutral *salts* only those of the alkalis are soluble in water; the solutions have an alkaline reaction. Most of the selenites are readily soluble in nitric acid, but the lead and silver salts dissolve with difficulty. The hydrogen selenites (biselenites) are soluble in water.

4. *Hydrogen sulphide* (in the presence of hydrochloric acid) produces in a solution of selenious acid or its salts a precipitate (*yellow* in the cold, and *reddish-yellow* on heating), consisting of a mixture of finely divided selenium and sulphur, which is *soluble* in *ammonium sulphide solution.*

5. *Barium chloride* produces (after neutralisation of any free acid present) a white precipitate of *barium selenite*, which is soluble in hydrochloric or nitric acid.

6. *Reducing agents* [1] readily effect a separation of *elementary selenium.* For example, *sulphur dioxide* precipitates from acid solutions, including those in sulphuric acid (distinction from tellurium), a *flocculent red precipitate* of selenium. In like manner *hydrazine sulphate* precipitates selenium, but not tellurium, from a tartaric acid solution (Pellini, *Zeitsch. anal. Chem.*, **50**, 521). *Stannous chloride* produces a precipitate of the same character both in hydrochloric and sulphuric acid solutions. *Acetylene* is also a very suitable reagent, since it rapidly precipitates very small quantities of selenium from the solutions of both tetravalent and hexavalent selenium (which latter, for example, are only slowly reduced by sulphur dioxide) (Jouve, *Chem. Zentr.*, 1901, I., 1389). *Ferrous sulphate* precipitates selenium rapidly and completely from strongly (hydrochloric) acid solutions. (Distinction from tellurium.) (Keller, *Chem. Zentr.*, 1897, II., 1092 [2].) *Metallic copper*, when introduced into a hot hydrochloric acid solution containing selenous acid, is immediately coated with a black deposit. If the liquid is allowed to stand for some time over the copper, it becomes light red, owing to the separation of selenium (Reinsch). Selenous acid thus behaves towards reducing agents in a manner very similar to that of sulphurous acid, but is oxidised with much more difficulty (*cf.* 9).

7. *Magnesia mixture* gives with selenious acid, usually after some time, a crystalline colourless precipitate of magnesium selenite, which is insoluble in acids (Hilger, v. Gerichten).

8. *Codeine and sulphuric acid* give a green coloration with selenous acid. This is a sensitive reaction, suitable for the detection of small amounts of selenium in sulphuric acid (Ernst Schmidt, *Chem. Zentr.*, 1911, II., 894).

9. *Selenium trioxide* (selenic anhydride), SeO_3, is formed on treating

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[1] With regard to the differentiation of hydrogen selenide and hydrogen arsenide liberated from an acid solution by means of *zinc*, see p. 347, footnote 1.

[2] See also Meyer and Jannek (*Zeitsch. anal. Chem.*, **52**, 531), who add solid sodium hydrosulphite, $Na_2S_2O_4$, to the slightly acid solution. They also confirm the statement of Schulz that petroleum gives a brown coloration with sulphuric acid containing selenium.

selenious acid with chlorine or bromine, or by heating selenium compounds with *alkali carbonates* and *nitrates*. The fused mass is dissolved in water, the solution is acidified with hydrochloric acid (remaining clear), and is then boiled, whereby chlorine is evolved, and the selenic acid converted into selenious acid.

10. *Selenic acid*, or rather, its ion, gives with barium chloride a white precipitate of barium selenate, which dissolves with difficulty in acids.

11. *Hydrogen sulphide* does *not* produce a precipitate in solutions of selenic acid. After boiling the liquid with hydrochloric acid, the resulting selenious acid is, of course, precipitated by hydrogen sulphide.

12. A *sulphuric acid solution of indigo* is *decolorised* by selenic acid.

13. When selenium or selenium compounds are fused with *potassium cyanide* in a *current of hydrogen*, *selenium potassium cyanide* is formed; selenium is *not* separated from this salt by the *action of air* (as in the case of tellurium), but is precipitated on boiling the solution for some time after the addition of hydrochloric acid.

14. When examined by Bunsen's method (p. 88), selenium compounds impart a *bright blue coloration to the flame*, whilst on volatilisation and combustion of the vapour the above-mentioned repulsive odour of selenium will be produced. The reduction product is brick-red to cherry-red, and when treated with concentrated sulphuric acid gives a dirty green solution. The oxide deposit is white, and when touched with a rod dipped in stannous chloride solution becomes red, owing to the separation of selenium.

15. Sodium selenide is formed on charcoal sticks, and this, when moistened on silver, yields *black silver selenide*, and on treatment with acid produces hydrogen selenide.

16. When heated with *sulphur iodide* on a block of gypsum in the oxidation flame of the blowpipe, selenium dioxide yields a reddish-brown deposit (Wheeler and Ludeking. *Cf.* also footnote on p. 389).

17. With regard to the *microchemical detection* of selenium, see Haushofer, *Mikroskopische Reaktionen*, p. 116; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 152; Heyn and Bauer, *Zeitsch. anal. Chem.*, **50**, 506; Denigès, *Chem. Zentr.*, 1916, I., 487.

Sec. 96.

4. Tellurium, Te, 127·5.

1. *Tellurium* is *divalent*, *tetravalent*, and *hexavalent*. It occurs in the elementary condition, alloyed with other metals, and, in small quantity and not widely distributed, as tellurium dioxide. The specific gravity of the different modifications of elementary tellurium ranges from 5·93 to 6·25.

Tellurium is a brittle, white metal, which is easily fusible (about 450°), and can be sublimed in a glass tube. When heated in the air it burns with a greenish-blue flame, emitting a thick white smoke of dioxide. Tellurium is insoluble in hydrochloric acid, but dissolves readily in nitric acid to form tellurium dioxide or nitrate. Powdered tellurium dissolves in concentrated sulphuric acid to form a purple solution, from which, on dilution with water, the tellurium is re-precipitated. On heating the concentrated solution it is decolorised, and most of the tellurium sulphate formed is precipitated.

2. Tellurium dioxide, TeO_2 (tellurous anhydride), is white, melts to a yellow liquid when heated to incipient redness, and volatilises when strongly ignited in the presence of air, but does not form a crystalline sublimate. It dissolves readily in hydrochloric acid, but less readily in nitric acid and dilute sulphuric acid, is easily soluble in potassium hydroxide solution, more slowly in ammonia solution, and is practically insoluble in water.

3. Tellurous acid, H_2TeO_3, is white, appreciably soluble in cold water, and readily soluble in hydrochloric and nitric acids. It is re-precipitated from its solutions in acids on the addition of water. Practically the whole of the tellurium separates after some time as crystalline dioxide from the nitric acid solution.

4. *Alkali hydroxides* and *carbonates* precipitate *tellurous acid* as a white precipitate, soluble in excess of the precipitant, from hydrochloric acid solutions of tellurium.

5. *Hydrogen sulphide* produces in acid solutions a *red precipitate* of tellurium sulphide, TeS_2, which rapidly *turns brown* (the colour resembling that of stannous sulphide), and when heated becomes black. This precipitate readily decomposes into tellurium and sulphur, so that possibly it may invariably be only a mixture of these two substances. It dissolves very readily in *ammonium sulphide solution*.

6. *Reducing agents*,[1] such as *stannous chloride* or *zinc*, precipitate *black metallic tellurium* from acid solutions. *Sulphur dioxide* and *sodium sulphite* only precipitate it in the presence of hydrochloric acid. If, however, the hydrochloric acid is concentrated, tellurium is *not* precipitated by sulphur dioxide. (Distinction from selenium.)

7. On heating a solution of tellurous acid in excess of potassium or sodium hydroxide solution with dextrose, tellurium is also precipitated in metallic form (Stolba).

8. *Ferrous sulphate* does *not* precipitate tellurium. (Distinction from selenium.)

9. Tellurous acid gives a *white precipitate* with *magnesia mixture*. This precipitate is not crystalline. (Distinction from selenious acid.) (Hilger, v. Gerichten.)

10. *Disodium hydrogen phosphate* gives a *white precipitate*, as does also *barium chloride*.

11. *Tellurium trioxide* (telluric anhydride), TeO_3, is formed by fusing tellurium or compounds of tetravalent tellurium with alkali nitrates and carbonates. The fused mass is soluble in water, and the solution remains clear when acidified with hydrochloric acid in the cold, but *when boiled* it

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[1] *Hydrazine sulphate* does *not* precipitate tellurium from a slightly acid solution containing excess of ammonium tartrate (distinction from selenium), whilst *hydrazine chloride* precipitates tellurium as well as selenium (Pellini, *Zeitsch. anal. Chem.*, **50**, 521).

evolves chlorine, tellurous acid being formed, and it then yields a precipitate *on the addition of water*, provided that the excess of acid is not too great. On oxidising tellurites with hydrogen peroxide, and adding concentrated nitric acid, a precipitate of telluric acid, or its hydrates, is obtained. Telluric acid is only a relatively weak acid, and shows a correspondingly slight resemblance to sulphuric acid and selenic acid.

Only the *alkali* tellurates are soluble in water.

12. *Hydrogen sulphide* produces in hot solutions of *hexavalent* tellurium a precipitate of the same composition as in solutions of tetravalent tellurium. *No precipitate is formed in the cold.* (Means of separating tellurium from heavy metal ions. Brauner and Kuzma, *Ber.*, 40, 3362.)

13. When tellurium, tellurium sulphide, or an oxygen compound of tellurium is fused with *potassium cyanide* in a *current of hydrogen*, *potassium telluride* is formed. The fused mass is soluble in water, but the whole of the tellurium is precipitated from the solution by means of a current of air. (Distinction and means of separation from selenium.)

14. If finely-powdered tellurium or a tellurium ore, *e.g.* gold telluride, is treated with a little water in a porcelain basin, a little metallic *mercury* introduced, and *sodium amalgam* added to the latter, the water will immediately assume a fine violet colour, owing to the solution of sodium telluride (G. Kustel).

15. When examined by Bunsen's dry method (p. 88 *et seq.*), tellurium compounds produce a pale blue coloration in the upper reduction area of the flame, while the oxidation area above appears *green*. The volatilisation is not accompanied by any odour. The reduction deposit is black, extending into a blackish-brown film; when heated with concentrated sulphuric acid, it gives a carmine-red solution. The oxidation deposit is white, and hardly perceptible; when treated with stannous chloride, it becomes black through the separation of tellurium.

16. When heated with sodium carbonate on *charcoal sticks*, tellurium compounds yield *sodium telluride*, which, when moistened on bright silver, produces a *black stain*; and, if much tellurium is present, emits the odour of hydrogen telluride when treated with hydrochloric acid, while tellurium is separated.

17. With regard to the *microchemical detection*, see Haushofer, *Mikroskopische Reaktionen*, p. 121; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 151; Heyn and Bauer, *Zeitsch. anal. Chem.*, **50**, 506; Denigès, *Chem. Zentr.*, 1916, I, 487.

For the *separation of selenium from tellurium*, the solution of tellurous and selenious acids in concentrated sulphuric acid is heated for some time with four times its volume of a moderately strong aqueous solution of sulphur dioxide, the precipitated selenium filtered off, and the filtrate heated with hydrochloric acid, with the addition of more sulphurous acid, to precipitate the tellurium (Divers and Schimosé). Or the selenium is precipitated from a solution in *strong* hydrochloric acid by means of sulphur dioxide, the filtrate diluted with water, and the tellurium precipitated in the same way (Keller, *Chem. Zentr.*, 1900, II., 143). The two elements may also be separated by means of ferrous sulphate. *Cf.* also footnote 1 on p. 384, and Sec. 95, 6.

In addition to this, a method of separating selenium from tellurium may be based upon the behaviour of an aqueous solution of the product of fusion with potassium cyanide when a current of air is passed through it; tellurium is precipitated, while selenium remains in solution.

SEC. 97.

5. Molybdenum, Mo, 96·0.

Molybdenum is *divalent, trivalent, tetravalent, pentavalent,* and *hexavalent.* It is of fairly rare occurrence, and only in moderate quantities, principally as sulphide (molybdenum glance) and lead molybdate (yellow lead ore).

1. Molybdenum is white (like tin), hard, and oxidisable when heated in the air. It is readily soluble in nitric acid and *aqua regia,* and also in concentrated sulphuric acid. It is exceedingly difficult to melt (at about 2250°). Its specific gravity is 9·1.

2. *Molybdanous oxide,* MoO, and the *sesquioxide,* Mo_2O_3, are black, whilst the *dioxide,* MoO_2, is dark brown or dark violet. All these oxides[1] when heated in the air or treated with nitric acid are converted into the *trioxide, molybdic anhydride,* MoO_3. This is a porous, white mass (becoming yellow when heated), which can be distributed as fine scales in water, and is then dissolved to a slight extent. It melts at a red heat, volatilises at a very high temperature in closed vessels, but even at a red heat in the air, and sublimes in transparent leaves and needles. When ignited in a current of hydrogen, it yields first the oxide and finally, after long and continuous ignition, the metal. Non-ignited molybdenum trioxide is soluble in acids, and in solutions of the hydroxides or carbonates of the alkali metals, with the formation of salts; after ignition it can be rendered soluble by fusion with alkali carbonate; it is also readily soluble in ammonia and alkali hydroxide solutions. When heated to redness in carbon tetrachloride or in a mixture of chlorine and carbon monoxide, molybdenum trioxide yields chlorides which can be sublimed (Quantin).

3. *Molybdic acid,* H_2MoO_4, is white; it dissolves with difficulty in water, and is precipitated from solutions of its salts by the careful addition of water; it is soluble in excess of acid. A *yellow* modification, H_2MoO_4,H_2O, separates under certain conditions from nitric acid solutions of ammonium molybdate on standing.

4. Solutions containing the ions of hexavalent molybdenum are

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[1] Acid solutions which contain molybdenum ion with valency corresponding to these oxides give precipitates with alkali hydroxides, carbonates, and phosphates, and also with ferro- and ferricyanides. The precipitates produced by carbonates are partly soluble in excess of the precipitant. Hydrogen sulphide and ammonium sulphide have the same action as in the case of hexavalent molybdenum.

colourless; a hydrochloric acid solution becomes coloured, speedily on contact with *zinc*, and immediately when treated with *stannous chloride*, owing to reduction, the coloration being blue, green, or brown, according to the reciprocal proportions and concentration of the substances. When digested with *copper* a sulphuric acid solution becomes blue, and a hydrochloric acid solution brown. The reaction often only takes place after some time. A solution of *ferrous sulphate*, acidified with sulphuric acid, produces a permanent blue coloration in acid solutions. On adding *sodium hypophosphite* and *sulphur dioxide* to an acid solution of molybdic acid, a blue precipitate or only a blue coloration of the liquid is produced, according to the amount of molybdenum present. Slight heat accelerates the appearance of the reaction (Millard). Many other reducing agents bring about reactions analogous to those just described.[1]

5. If a little concentrated sulphuric acid is dropped on to a piece of indented platinum foil, or if a few drops of sulphuric acid are placed in a porcelain dish, and a small quantity of powdered molybdic trioxide or a molybdate is added, the mixture heated until copious fumes appear, and then cooled and treated with a little *alcohol* (or repeatedly *breathed upon*), the sulphuric acid will assume an *intense blue coloration* (v. Kobell, Schön, Maschke). In the presence of antimony pentoxide and a large amount of stannic oxide, the mixture must be evaporated to dryness with phosphoric acid before heating it with sulphuric acid (Maschke). If vanadic acid is present, a green coloration is produced (Truchot, *Chem. Zentr.*, 1905, I, 573).

6. *Potassium ferrocyanide* produces a *red-brown precipitate* in solutions acidified with hydrochloric acid.

7. *Extract of gall nuts*, and also *tannin*, gives a *deep red coloration*, shading into *brown*, with solutions of alkali molybdates. If hydrochloric acid is added, a brown precipitate or coloration is produced.

8. The addition of a little *hydrogen sulphide* gives a *blue coloration* with acid solutions, whilst a larger amount produces a brownish-black precipitate. The supernatant liquid over the precipitate appears green at first. After the liquid has stood for a time, and is then heated and repeatedly treated with hydrogen sulphide, the whole of the molybdenum is precipitated, although with some difficulty, as *brownish-black trisulphide*, MoS_3. Complete precipitation is effected by saturating the solution with hydrogen sulphide, and then heating it in a closed pressure-flask. *The precipitate is soluble in alkali sulphide solutions.* Acids precipitate molybdenum sulphide from the resulting sulpho salt solutions, the precipitation being promoted by heat. *Solutions of alkali molybdates* give a yellow coloration with *hydrogen sulphide*, and then, on the addition of acids, a *brownish-black precipitate*. On treating a solution of molybdic acid in excess of ammonia solution with yellow *ammonium sulphide solution* (containing polysulphides), and boiling the liquid for some time, there is produced, in addition to a *brownish-black precipitate*, an *intense dark red*

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[1] *Cf.* for example Kafka, *Zeitsch. anal. Chem.*, **51**, 482, and Pozzi Escot, *Chem. Zentr.*, 1913, II., 85; 1914, I., 76.

solution, provided that the ammonium sulphide is not present in too great excess. Boiling *oxalic acid solution* does not attack molybdenum sulphide (Method of separation from the sulphide prepared by the wet method, which is soluble therein. Clarke.) When ignited in the air or heated with *nitric acid*, molybdenum sulphide is converted into molybdenum trioxide.

9. On treating a solution containing molybdate ion with potassium thiocyanate and a little hydrochloric acid, it becomes *yellow*, and on then adding *zinc*,[1] reduction takes place, and this leads to the formation of a molybdenum thiocyanate, corresponding to the oxide or sesquioxide. The liquid becomes *carmine-red* through this reaction, and the coloration is not destroyed by the addition of *phosphoric acid*. (Distinction from ferric thiocyanate.) On shaking the red liquid with ether, the thiocyanates are extracted, and a red ethereal layer is obtained (C. D. Braun).[2] Tartaric acid and other organic acids prevent the reaction, owing to the formation of complex compounds.

10. On treating an acid solution of molybdic acid with *hydrogen peroxide*, a *yellow liquid is obtained*, the colour of which is *not* removed by shaking with ether. Ammoniacal solutions become reddish-brown on treatment with hydrogen peroxide, owing to the formation of ions of ammonium permolybdate (Schön, Werther, Barwald, Bettel, Melikow, *Chem. Zentr.*, 1912, II., 1579; A. Komarowsky, *Ibid.*, 1913, II., 996). The reaction is not applicable in the presence of vanadates or titanates.

11. On adding an acetic acid solution of phenylhydrazine to a solution containing molybdic acid, and heating the liquid to boiling point, an intense *wine-red coloration* or a *red precipitate* is obtained. The red substance may be extracted by shaking with chloroform. This is a very sensitive reaction (Spiegel and Maass, *Ber.*, **36**, 512). When added to an ammoniacal solution, phenylhydrazine acetate produces a coloration resembling that of *wine yeast*, or a precipitate of the *same colour*. If a little *tannin solution* has been previously added, the colour becomes *mahogany brown* (Pozzi Escot, *Chem. Zentr.*, 1907, I., 1160).

12. An alcoholic solution of *diphenyl carbazide* produces a *fine indigo-violet coloration* in a weak solution of alkali molybdate, or a precipitate of the same colour if excess of the reagent is added. The coloration is destroyed by an excess of acid or alkali. If, instead of ethyl alcohol, a homologous alcohol is used as the solvent for the diphenylcarbazide, other shades of colour are produced (Lecocq, *Chem. Zentr.*, 1904, I., 836).

13. With regard to the colorations which molybdenum chloride solutions give with *alkanet tincture* and their *absorption spectra*, see Formánek, *Zeitsch. anal. Chem.*, **39**, 680).

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[1] Or another reducing agent, such as *hydrogen sulphide*. This method is recommended by Ganassini for the detection of traces of molybdenum, the solid substance being triturated with a small amount of concentrated sulphuric acid containing a little potassium thiocyanate, and the liquid spread out and subjected to the action of a current of hydrogen sulphide.

[2] If the reduction of the molybdate ion is carried too far, the reaction may not take place (E. Kedesdy, *Chem. Zentr*, 1913, II., 996).

14. Molybdenum compounds impart a *yellow* to *brownish-yellow coloration* to *alkali phosphate beads*, while hot, in the *oxidation* flame, the beads becoming yellowish-green to colourless on cooling; in the *reduction flame* the beads are *dark brown* while hot, and *bluish-green* to *grass-green* after cooling. Similar, but much less pronounced, colorations are obtained with *borax* (Lutz, *Zeitsch. anal. Chem.*, **47**, 21).

15. Molybdenum trioxide volatilises when heated on charcoal in the *oxidation flame of the blowpipe*. The charcoal becomes coated with a yellow (frequently crystalline) powder, which changes to white on cooling. *Metallic molybdenum* is formed in the reducing flame, and by sedimentation with water is obtained as a grey powder. Molybdenum sulphide yields sulphur dioxide in the oxidising flame, and forms a deposit of molybdenum trioxide on the charcoal.

16 On heating molybdenum trioxide or a molybdate for a short time with *sodium carbonate* in a platinum spiral, dissolving the fused mass in a few drops of hot water, and absorbing the solution in strips of filter paper, the molybdenum may be detected in these by means of spotting tests with hydrochloric acid and potassium ferrocyanide, with stannous chloride, and with ammonium sulphide and hydrochloric acid (Bunsen).

17. On heating molybdenum trioxide with an equal quantity of sulphur iodide [1] on an artificially-made tablet of gypsum in the oxidising flame of the blowpipe, an *ultramarine-blue deposit* will be obtained (Wheeler and Ludeking).

18. With regard to the *microchemical detection of molybdenum*, see Haushofer, *Mikroskopische Reaktionen*, p. 97; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 145.

SEC. 98.

6. Tungsten, W, 184·0.

Tungsten is *divalent*, *tetravalent*, *pentavalent*, and *hexavalent*. It is not widely distributed in nature, and is not found in any large quantities. The tungsten minerals of most common occurrence are scheelite or tungstone (calcium tungstate) and wolframite (ferrous and manganous tungstate).

1. *Tungsten*, as obtained by reducing the trioxide with aluminium or hydrogen at a high ignition temperature, is an iron-grey powder of sp. gr. 19·1, melting with great difficulty at 2850°. Pulverulent tungsten, when ignited in the air, is converted into tungsten trioxide (tungstic anhydride), WO_3, and, when ignited in a current of dry chlorine free from air, yields a sublimable blackish-violet chloride, WCl_6, which usually contains lower chlorides and sometimes oxychlorides. On heating the chloride with water it is decomposed with the formation of tungstic acid. Tungsten chloride is also obtained by heating the trioxide to redness in a current of

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[1] This is prepared by fusing 10 parts of iodine with 60 parts of sulphur and powdering the fused mass.

carbon tetrachloride vapour, or in a mixture of chlorine and carbon monoxide (Quantin). On igniting the trioxide in a current of hydrogen chloride, volatile chlorides are obtained (Friedheim, Henderson, and Pinagel, *Zeitsch. anorg. Chem.*, **45**, 396; *Zeitsch. anal. Chem.*, **48**, 190). Tungsten is insoluble, or practically insoluble, in acids, including *aqua regia*. Even hydrofluoric acid by itself hardly dissolves it, but it is fairly easily soluble in a mixture of nitric and hydrofluoric acids (Moissan, *Chem. Zentr.*, 1896, II., 416). It is not dissolved by potassium hydroxide solution, but is soluble in a solution of potassium hydroxide which has been treated with alkali hypochlorite. When fused with potassium hydroxide, tungsten is slowly dissolved, while hydrogen is liberated. Very finely divided tungsten is soluble even in ammonia and hydrogen peroxide solutions, or in a solution of ammonium persulphate. A coarser powder may be oxidised by ignition after moistening with nitric acid, and the oxidation product then extracted with a solution of sodium hydroxide and hydrogen peroxide. Tungsten, even in comparatively large fragments, may be rendered soluble by fusion with alkali nitrite (Hans Arnold, *Zeitsch. anorg. Chem.*, **88**, 74; *Chem. Zentr.*, 1914, II., 1124; *Zeitsch. anal. Chem.*, **54**, 357).

2. *Tungsten oxide*, WO_2, is brown; when strongly ignited in the air it is converted into the trioxide. *Tungsten trioxide*, WO_3, is lemon-yellow, becoming dark orange when heated, is not decomposed by heat, and is insoluble in water and acids. A series of *hydroxides* corresponds to the trioxide, some of which have both a slightly basic as well as a definite acid character. These include *tungstic* acids, H_2WO_4, which is yellow, and H_2WO_5, which is white, and *metatungstic acid*, $H_4W_4O_{13}$. They all show a pronounced tendency to change into the colloidal condition.

3. Several series of *salts*, therefore, correspond to these acids. On fusing tungsten trioxide with *potassium hydrogen sulphate*, and treating the fused mass with water, there is at first obtained an acid solution, which does not contain any tungsten ions.[1] After separation of the solution, the residue, consisting of *potassium tungstate* with a large excess of tungstic acid, will dissolve completely in water to which *ammonium carbonate* has been added. (Distinction and means of separation from silicon dioxide.) On fusing the trioxide with *alkali carbonates* or *sodium peroxide*, *alkali* tungstates[2] are obtained; these dissolve readily in water, and with more difficulty when boiled with alkali carbonate solutions.

4. *Hydrochloric*, *nitric*, or *sulphuric acid*, when added in sufficient quantity, produce *white precipitates of hydrated tungstic acid in solutions of alkali tungstates.* When boiled, the precipitates *become yellow and lose water*, and they are *insoluble in excess of the* acids. (Distinction from

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[1] Because the potassium hydrogen sulphate present prevents them from dissolving.

[2] Metallic tungsten and tungsten trioxide are rendered soluble by fusion with potassium nitrate and potassium carbonate at a temperature below red heat. (Method of separation from titanium.) (Defacqz, *Chem. Zentr.*, 1897, I., 129.)

molybdic acid.) The tungstic acids are soluble, however, in very concentrated hydrochloric acid. *They do not volatilise when heated with hydrofluoric acid and a little sulphuric acid* (distinction from silicon dioxide), *but are soluble in ammonia solution. They dissolve*, after decantation of the acids, even in water, if the treatment is continued long enough. On evaporating them to dryness with excess of nitric acid, heating the residue to 120°, and treating it when cold with a solution of ammonium nitrate containing nitric acid, the residue will contain almost the whole of the tungstic acid (N. J. Tram, A. Ziegler). Phosphoric acid does not cause a precipitation. It even prevents the precipitation by other acids,[1] owing to the formation of complex compounds.[2]

5. *Barium chloride, calcium chloride, lead acetate,*[3] *silver nitrate*, and *mercurous nitrate* produce *white* precipitates in solutions of tungstates.

6. *Potassium ferrocyanide* produces a deep brownish-red coloration on the addition of a little acid, and after some time a *precipitate of the same colour is formed.*

7. *Gall-nut tincture* or *tannin* gives a brown coloration or precipitate on the addition of a little acid.

8. *Hydrogen sulphide* produces scarcely any precipitate in acid solution. *Ammonium sulphide* does *not* give a precipitate with a solution of alkali tungstate. In the presence of ions which can be precipitated by ammonium sulphide, *e.g.* manganous ion (Taggart and Smith, *Chem. Zentr.*, 1897, I., 309), tungsten sulphide may be partially precipitated at the same time. *On acidifying a solution containing excess of ammonium sulphide a pale brown precipitate of tungsten sulphide*, WS_3, mixed with sulphur, will be precipitated; this is somewhat soluble in pure water, but is barely soluble in water containing salts.

9. *Stannous chloride* produces a *yellow precipitate* in solutions of alkali tungstates; on adding hydrochloric acid, and heating the tube, the precipitate will become *bright blue*. This is a very sensitive and characteristic reaction, which is suitable for the separation of tungstate ion from molybdate ion (Marbaker, *Zeitsch. anal. Chem.*, 56, 110).

10. On treating a solution of an alkali tungstate with concentrated hydrochloric acid, or better, with excess of *phosphoric acid*, and adding zinc, a *bright blue coloration* will be produced. The blue coloration obtained

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[1] Tungstic acid may be precipitated by adding *tannic acid* and *ammonia* in the presence of phosphate ion and subsequently acidifying the liquid with concentrated *hydrochloric acid* (Barber, *Monatsh. Chem.*, **27**, 379; *Chem. Zentr.*, 1906, II., 763).

[2] With regard to the separation of phosphate ion from tungstate ion in such solutions, see v. Knorre, *Zeitsch. anal. Chem.*, **47**, 37 (and for the separation of tungstate ion from chromate, *Ibid.*, **47**, 337); also Kehrmann, *Ber.*, **20**, 1813; *Zeitsch. anal. Chem.*, **27**, 392 (also for the separation of the ions of arsenic and tungsten); Kehrmann, *Liebig's Ann.*, **245**, 45; *Zeitsch. anal. Chem.*, **39**, 717.

[3] The resulting precipitate is soluble, after ignition, in concentrated hydrochloric acid, but separates again on diluting the solution with water. (Distinction from molybdate ion. Ibbotson and Brearley, *Chem. Zentr.*, 1900, I., 490.)

in hydrochloric acid solution changes first into red and then into brownish-black. A liquid of deep blue colour [1] is also produced by gently heating a solution of alkali tungstate (slightly acidified with sulphuric acid) to which *sodium hypophosphite* and *sulphur dioxide* have been added.

11. *Ferrous sulphate* produces an *ochre-yellow precipitate*, which does *not* become *blue on the addition of acids*. (Distinction from molybdate ion.)

12. *Tartaric*, *citric*, and many other *organic acids* form complex compounds with tungstic acid. Hence these acids do *not* precipitate tungstic acid from tungstate solutions, and even prevent its precipitation by mineral acids. For the same reason, they interfere more or less with the action of the reducing agents just mentioned, and the consequent production of a *blue coloration*.

13. On heating tungsten trioxide with *potassium hydrogen sulphate* and a little concentrated sulphuric acid, allowing the mixture to cool, and adding a drop of a *phenol*, *characteristic colorations* (usually disappearing on the addition of water) are obtained. For example, phenol produces a red, and hydroquinone a violet coloration (Defacqz, *Chem. Zentr.*, 1896, II., 639).

14. Most of the *metatungstates* are *soluble* in water. Ordinary tungstic acid is precipitated on boiling the solutions with *sulphuric*, *hydrochloric*, or *nitric acid*.

15. *Alkali phosphate* dissolves tungstic trioxide or tungstates. In the oxidising flame the beads are transparent and colourless or yellow, whilst in the reducing flame they appear bright blue, the colour becoming blood-red on the addition of ferrous sulphate. *Borax beads* do not show any characteristic coloration.

16. On heating tungsten compounds with very little *sodium carbonate* in a hollow on charcoal in the *inner blowpipe flame*, tungsten powder, which can be separated by sedimentation, is obtained.

17. When tungstates are heated with sodium carbonate in a platinum spiral, the fused mass heated with a few drops of water, and the solution absorbed by means of strips of filter paper, tungsten may be detected in these by a *yellow coloration* when they are heated after the addition of a drop of *hydrochloric acid*, and by a *blue coloration* when they are heated with a drop of *stannous chloride solution*. *Ammonium sulphide* does not colour the paper either by itself or after the addition of hydrochloric acid, but when heated the paper becomes blue or green (Bunsen).

18. When heated with *sulphur iodide* on a gypsum tablet in the *oxidising flame of the blowpipe*, tungstates yield a greenish-blue deposit (Wheeler and Lüdeking). See also footnote, p. 389.

19. Most of the tungstates insoluble in water may be *decomposed by digestion with acids*. The mineral wolframite, which is only attacked by acids with difficulty, may be decomposed by fusion with *alkali carbonate*

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[1] Other reducing agents also produce a blue coloration, such as mercurous nitrate and potassium iodide (Katka, *Zeitsch. anal. Chem.*, **51**, 482), or mercury (Pozzi-Escot, *Chem. Zentr.*, 1913, II., 85 : 1914, I., 76).

or *sodium peroxide*. The fused mass is soluble in water. Metallic tungsten and tungsten alloys (ferrotungsten) may conveniently be dissolved in *hydrofluoric acid with nitric acid*, the solution then treated with sulphuric acid, and the volatile acids evaporated (Ibbotson and Brearley, *Zeitsch. anal. Chem.*, **44**, 561). On treating tungsten steel with hydrochloric acid, metallic tungsten separates, and may be dissolved by adding nitric acid. For the analysis of metallic tungsten, H. Arnold (*Zeitsch. anorg. Chem.*, **88**, 71; *Zeitsch. anal. Chem.*, **54**, 357) recommends dissolving the powder, if fine, directly in ammonia and hydrogen peroxide solution, or if coarse, in sodium hydroxide and hydrogen peroxide solution, after oxidation with nitric acid, whilst larger pieces may be electrolytically dissolved as anodes in ammonia solution. The alkaline or ammoniacal solution is treated with 50 per cent. tartaric acid solution, and then with hydrochloric acid, until the solution contains 4 per cent. of that acid, after which the liquid is saturated with hydrogen sulphide and filtered, and the filtrate poured in a thin stream into boiling strong hydrochloric acid. Most of the tungstic acid will then separate as a granular precipitate. The filtrate is evaporated to dryness, the residue ignited, whereby the tartrates are converted into carbonates, and the resulting fused mass is extracted with water. Oxides or carbonates of Groups III. and IV. remain in the residue, whilst tungstic acid is dissolved.

20. With regard to the *microchemical detection* of tungsten, see Haushofer, *Mikroskopische Reaktionen*, p. 141; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 124.

B. Reactions of the Anions.

SEC. 99.

Reagents for the determination of the anions, analogous to the reagents for the detection of the cations, can be divided into *general group reagents* and *special reagents*, *i.e.* those which serve to identify individual anions. It is, however, hardly possible to arrange and define the groups as sharply as was the case with the cations.

Acids are divided into two main groups, *inorganic* and *organic* acids. For analytical purposes, deviating from the theoretical conception, we make the divisions in such a way that the differentiation is based on the behaviour at a higher temperature, and *include in the organic acids only those the salts of which* (especially those with the ions of alkalis or alkaline earths) *are decomposed on ignition, with the separation of carbon*. This characteristic has the advantage that it is very evident, and that by means of a simple preliminary test it renders it more easy to determine to which division the acid should belong. The salts of *organic* acids with *alkali* or *alkaline earth metals* are converted on gentle ignition into *carbonates*.

The *inorganic anions* can be divided into three groups, according to their behaviour towards the group reagents, *barium chloride* and *silver nitrate*, the first of which can again be subdivided into four classes, according to the behaviour of the members of the group towards (*a*) *hydrogen sulphide*, and (*b*) of their *barium salts towards acids*.

The *organic anions* dealt with in this book can be divided firstly into two groups, according to their behaviour towards *calcium chloride*, and each of these is again sub-divided into two divisions.

The first group is characterised by its behaviour towards *ferric chloride*, and the second by the *condition of aggregation*, the *volatility*, and the *solubility of the free acids*.

As in the case of the cations, a general survey of all the anions contained in this book will precede the description of the individual ones. Here again the more frequent and important members of the groups are printed in italics.

The behaviour towards the group reagents is in each case given at the beginning of each group or sub-division.

I. Inorganic acids.

First Group.

First division. *Chromic acid* or *chromate ion* (sulphurous acid, thiosulphuric acid, and iodic acid, or sulphite, thiosulphate, iodate ions).

Second division. *Sulphuric acid* or *sulphate ion* (persulphuric acid or persulphate ion, silicohydrofluoric acid or silicofluoride ion).

Third division. (Ortho-, pyro-, and meta-) *phosphoric acid*, *boric acid* (perboric acid), *oxalic acid*, *hydrofluoric acid*, or *phosphate ion*, *borate ion* (perborate ion). *oxalate ion*, *fluorine ion* (phosphorous acid or phosphite ion).

Fourth division. *Carbonic acid* (percarbonic acid), *silicic acid*, or *carbonate ion* (percarbonate ion), *silicate ion*.

Second Group.

Hydrochloric acid, *hydrobromic acid*, *hydriodic acid*, *hydrocyanic acid*, *hydroferrocyanic acid*, *hydroferricyanic acid*, *thiocyanic acid*, *hydrogen sulphide*, or *chlorine*, *bromine*, *iodine*, *cyanogen*, *ferrocyanogen*, *ferricyanogen*, *thiocyanogen* and *sulphide ions* (nitrous, hypochlorous, hypophosphorous, nitrosulphuric acids, or nitrite, hypochlorite, hypophosphite, and azide ions).

Third Group.

Nitric acid, chloric acid, or *nitrate, chlorate ions* (perchloric acid or perchlorate ion).

II. Organic acids.

First Group.

First division. *Oxalic acid, tartaric acid* (racemic acid), *citric acid, malic acid,* or *oxalate, tartrate* (racemate), *citrate, malate ions.*

Second division. *Succinic acid, cinnamic acid,* or *succinate ion, cinnamylate ion.*

Second Group.

First division. *Benzoic acid, salicylic acid,* or *benzoate ion, salicylate ion.*

Second division *Acetic acid, formic acid,* or *acetate ion, formate ion* (lactic acid, propionic acid, butyric acid, or lactate, propionate, butyrate ions).

IV. REACTIONS OF INDIVIDUAL ANIONS.

A. Inorganic acids.

SEC. 100.

First Group.

Anions which are precipitated by barium chloride from neutral solutions.

This group is divided into four classes, as follows: —

(*a*) Acids *which are decomposed by the action of hydrogen sulphide on their acid solution,* and which were, therefore, referred to in the examination of cations, *i.e.* chromic acid (sulphurous acid and thiosulphuric acid — the latter, because it is decomposed and recognised at once on the addition of hydrochloric acid to the solution of one of its salts —and also iodic acid [1]).

(*b*) Acids which are not decomposed by hydrogen sulphide in acid solution, and the *barium salts of which are insoluble or scarcely soluble in hydrochloric acid: sulphuric acid* (silicohydrofluoric acid).

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[1] The first division of the first group of acids should have included all oxygen compounds of pronounced acid characteristics which have already been dealt with in the sixth group of cations (arsenic acid, antimonic acid, selenious acid, etc.) As, however, their behaviour towards hydrogen sulphide formerly caused them to be grouped with other cations rather than with other acids, these compounds, which, at least from an analytical point of view, are on the borderline between cations and anions, *i.e.* acids, are described with the cations.

(*c*) Acids which are not decomposed by hydrogen sulphide in acid solution, and the *barium salts* of which *are apparently soluble in hydrochloric acid without decomposition,* in so far as the acids or their anhydrides are neither separated in solid form nor escape as a gas: *phosphoric acid, boric acid, oxalic acid, hydrofluoric acid* (phosphorous acid). (Oxalic acid is, in accordance with its chemical nature, also included among the organic acids, but is mentioned here because the behaviour of its salts, which are decomposed on ignition without actual carbonisation, causes it easily to be overlooked as an organic acid).

(*d*) Acids which are not decomposed by hydrogen sulphide in acid solution, *and the barium salts of which are soluble in hydrochloric acid, with the liberation of the acids or their anhydrides: carbonic acid, silicic acid.*

First Division.

Of the First Group of Inorganic Acids.

SEC. 101.

Chromic acid, H_2CrO_4, **and dichromic acid** (bichromic acid, pyrochromic acid), $H_2Cr_2O_7$ (chromate ion CrO''_4, or dichromate ion, $Cr_2O''_7$).

1. *Chromium trioxide*, chromic anhydride, CrO_3, forms a scarlet crystalline mass or distinct needle-shaped crystals. On ignition it decomposes into chromic oxide (Cr_2O_3) and oxygen. It deliquesces quickly in the air; it dissolves in water with a yellowish-dark red colour, visible even when considerably diluted. *Chromic acid* and *dichromic acid* are not known in the pure condition, but their existence may be assumed in the aqueous solution of the trioxide. Both are di-basic, *i.e.* correspond to the anions CrO''_4 and $Cr_2O''_7$.

Chromic acid in the first stage is a strong acid, in the second stage is very weak; for the dissociation constant K_2 for the process $[H^{\cdot}].[CrO''_4] = K_2.[HCrO'_4]$ is $= 3.7.10^{-7}$, that is to say, only of the order of dimension of the first dissociation constant of carbonic acid. Dichromic acid is stronger in both stages, but especially in the second, than chromic acid (see Beck and Stegmuller, *Arbeiten a. d. Kaiserl. Gesundheitsamt*, 34, 446).

2. The *chromates* and *dichromates* are all red or yellow, and mainly

insoluble in water. Some of them are decomposed on ignition. Chromates have a great resemblance to sulphates and manganates, with which some of them also crystallise isomorphously. There is, however, no hydrochromate ion analogous to the hydrosulphate ion. The alkali chromates K_2CrO_4 and Na_2CrO_4 resist the action of heat. Alkali chromates dissolve in water with a yellow colour, and alkali dichromates with a reddish-yellow colour. The colorations are visible even in very dilute solutions. The former have a neutral, the latter an acid reaction. On the addition of an acid, whereby the concentration of the $HCrO'_4$ ions is first of all increased, the yellow colour of a solution of chromate changes to reddish-yellow, owing to the formation of dichromate ion, $2HCrO'_4 \rightleftarrows Cr_2O''_7 + H_2O$. In neutral aqueous solutions the process is reversed. Dichromate ions are always decomposed to a certain degree into $HCrO'_4$ or also CrO''_4 ions, which, with suitable cations form precipitates of chromates, because chromates do not dissolve so readily as the corresponding salts of the stronger dichromate ion.

3. **Hydrogen sulphide** produces in the *acidified* solution of a chromate *at first a brownish*, and then, owing to the formation of a chromic salt, a green coloration of the solution, with the simultaneous separation of sulphur, which gives the liquid a milky appearance:

$$Cr_2O''_7 + 11H^{\cdot} + 3HS' = 2Cr^{\cdot\cdot\cdot} + 7H_2O + 3S$$

$$\text{e.g. } K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

Heat promotes the reaction, and part of the sulphur is then oxidised to sulphuric acid.

4. *Ammonium sulphide*, added in excess to a solution of *alkali dichromate*, at once produces a *brownish, grey-green precipitate* consisting essentially of chromic hydroxide and sulphur. In a *neutral solution of alkali chromate* there is at first only a dark brown coloration, but after a while a brownish grey-green precipitate similar to that just mentioned is separated. The precipitations are only complete after boiling. The precipitates dissolve after washing in hydrochloric acid and give off an odour of hydrogen polysulphide.

5. *Chromate ion may be reduced to chromic ion by the use of many other agents*, especially by *sulphur dioxide*, *ammonium thioacetate* in acid solution, *sodium thiosulphate* in acid solution, by heating with *concentrated hydrochloric acid*, also with *dilute hydrochloric acid* to which *alcohol is added* (whereby ethyl chloride and aldehyde escape), by *stannous chloride* or *metallic zinc* in the presence of hydrochloric or sulphuric acid, by heating with *tartaric acid*, *oxalic acid*, etc. All

these reactions are clearly characterised by the change from the red or yellow colour of the solution to the green or violet colour of the chromic salt. *Alkali chromate solutions* are *not reduced* by *alcohol* even when heated. (Distinction from manganates and permanganates.)

6. **Barium chloride** *produces in aqueous solutions of chromates and dichromates a yellowish-white precipitate of barium chromate*, $BaCrO_4$. It dissolves readily in dilute hydrochloric acid and nitric acid, as then, through the formation of dichromate ion (see 2) and of undissociated chromic acid or hydrogen chromate ion, the concentration of the CrO''_4 ions is so decreased, that the solubility product $[Ba^{\cdot\cdot}].[CrO''_4]$ is no longer reached. Barium chromate is scarcely soluble in cold, but dissolves more readily in boiling water. Ammonium salts increase the solubility very noticeably (see p. 141, 9) and acetic acid very considerably, but the salt is completely insoluble in these weaker solvents if neutral alkali chromate is added to the liquid. The reason for this lies in the fact that the hydrogen ions (also present in ammonium salts, owing to hydrolysis) are removed in the formation of dichromate ion ($2CrO''_4 + 2H^{\cdot\cdot}$ $Cr_2O''_7 + H_2O$) without any great reduction in the concentration of the chromate ions.[1]

7. **Silver nitrate** produces in an aqueous *neutral* solution of a chromate *a dark brownish-red precipitate of silver chromate*, Ag_2CrO_4, readily soluble in nitric acid and ammonia solution, and in *weak acid* solutions a *dark red to reddish-brown crystalline precipitate of silver dichromate*, $Ag_2Cr_2O_7$, which is readily soluble in ammonia solution but less easily in nitric acid.

8. **Lead acetate** precipitates *lead chromate*, $PbCrO_4$, from an aqueous or acetic acid solution of a chromate as a *yellow precipitate*, insoluble in ammonia solution, soluble in potassium and sodium hydroxide solutions, soluble with difficulty in dilute nitric acid, and insoluble in acetic acid. On heating with alkali hydroxide the yellow neutral salt is converted into a basic red one $(PbOPb)CrO_4$.

9. If a *quite dilute acid solution* of **hydrogen peroxide** (about 6 to 8 c.c.) is covered with a little *ether* (a layer of about ½ cm. in thickness) and a liquid containing chromate ion is added, the solution of hydrogen peroxide assumes a *bright blue colour*. If the test-tube, closed with the thumb, is reversed several times without much shaking, the solution loses its blue colour and *the ether becomes blue*. This latter phenomenon is especially characteristic. One

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[1] *Cf.* La Santi, *Chem. Zentr.*, 1904, II., 1625.

part of potassium chromate in 40,000 parts of water still gives a perceptible reaction (Storer); vanadic acid influences the sensitiveness of the reaction considerably (Werther, *J. prak Chem.*, **83**, 195), but if sodium phosphate is added, the injurious influence of the vanadic acid can be eliminated, owing to the formation of a complex acid. (Reichard, *Zeitsch. anal. Chem*, **40**, 577) The blue coloration is presumably due to perchromic acid, H_3CrO_8.[1] The formation of this acid takes place in accordance with the formula:

$$Cr_2O''_7+7H_2O_2=2CrO'''_8+4H^{\cdot}+5H_2O$$

or $$H_2Cr_2O_7+7H_2O_2=2H_3CrO_8+5H_2O$$

After a short time a reduction to chromic ion takes place, and consequently a decoloration of the ether:

$$2CrO'''_8+12H^{\cdot}=2Cr^{\cdots}+6H_2O+5O_2$$

for example

$$2H_3CrO_8+3H_2SO_4=Cr_2(SO_4)_3+6H_2O+5O_2$$

10. *Diphenylcarbazide*, or diphenylcarbazide acetate in alcoholic solution, if added in excess to chromic acid—or neutral or acid chromate solutions—produces a beautiful purple-violet coloration (Cazeneuve, *Chem. Zentr*, 1901, II, 709; *Zeitsch. anal Chem.*, **41**, 568); smaller quantities of the reagent produce red or brown colorations (Moulin, *Chem. Zentr*, 1904, I., 1175; *Zeitsch. anal. Chem*, **48**, 385).

11 *If insoluble chromates are fused with sodium carbonate*, with the addition of a little *potassium chlorate*, and the mass treated with water, a *solution, coloured yellow* by the chromate ion contained in it, is obtained, which becomes reddish-yellow when an acid is added. The metals are left in the form of oxides or carbonates.

12. Chromates are reduced to chromic compounds when heated with *phosphates* or *borax* in the oxidising or reducing flame, and then show the corresponding reactions. (Sec. 41, 13, p. 170.)

13. *Very small quantities of chromate ion* may be detected in aqueous solutions (but only in the absence of other oxidising substances) by one of the following methods:—(*a*) A little *guaiacum tincture* (1 part of the resin to 100 parts of alcohol 52 per cent. by weight) is added to the liquid slightly acidified with sulphuric acid; if a chromate ion is present an *intense blue coloration* is produced, which, however, disappears in a few seconds if the quantity of chromate is very small (H. Schiff). (*b*) A little diphenylamine is

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[1] The blue perchromates obtained by Riesenfeld and his collaborators correspond to this acid

dissolved in concentrated sulphuric acid, and a few drops of the liquid containing the chromate added. A distinct *blue coloration* will prove that chromate ion is present. (*c*) A small piece of starch moistened with freshly prepared *potassium iodide solution* is brought into contact with the chromate solution (acidified with dilute hydrochloric or sulphuric acid), or a dilute freshly prepared *potassium iodide solution* is mixed with a small quantity of carbon bisulphide, the chromate solution (acidified with hydrochloric or sulphuric acid) added, and the whole shaken. A *blue coloration of the starch*, or a *violet coloration of the carbon bisulphide* indicates the presence of the smallest trace of chromate ion. (*d*) The liquid under examination is acidified with a little sulphuric acid, and a small quantity of an aqueous solution of *pyrogallol-dimethyl ester* added. A *yellow-red coloration* indicates chromate ion In the case of very weak colorations the reaction can be made more distinct by shaking with chloroform, which extracts the colouring substance. This is a very sensitive reaction, but is not confined to chromate ion (Mayerfeld, *Chem. Ztg*., **34**, 918). (*e*) 5 c.c. of a solution of 0·5 grm of *α-naphthylamine* and 50 grms of tartaric acid (or instead, oxalic acid or glacial acetic acid, but not an inorganic acid) in 100 c c of water give a blue coloration with a solution of chromic acid. The reaction is still distinct at a concentration of 0 1 mgrm in 100 c c. It depends on the formation of an oxidation product of the α-naphthylamine Chlorine and bromine, like chromic acid, give a blue coloration. Nitric acid gives a red, ozone a violet, coloration Iodine, ferric chloride, nitrous acid and hydrogen peroxide do not give colorations (Van Eck, *Chem. Zentr.*, 1915, I., 399).

As chromate ion is reduced by hydrogen sulphide to chromic ion, it will have been already detected in the course of analysis in the tests for cations It may also be easily recognised by the intense colour of the solutions containing chromate ion, the excellent reaction with hydrogen peroxide, and the characteristic precipitates produced by lead and silver salt solutions. The reactions mentioned in 13 serve, after fusion of the substances with alkali carbonate and alkali chlorate, for the detection of the slight traces of chromium which are to be found in many minerals, *e.g.* serpentine.

For the detection of alkali chromates in the presence of dichromates, see E Donath (*Zeitsch. anal. Chem* ., **18**, 78), and also Richter (*Ibid.*, **21**, 368). With regard to the *microchemical detection* of chromic acid, see p. 170.

Acids of less Frequent Occurrence of the First Division.

SEC. 102.

Sulphurous acid, H_2SO_3 (Sulphite ion, SO''_3, Hydrogen sulphite or Hydrosulphite ion, HSO'_3).[1]

1. *Sulphur dioxide*, sulphurous anhydride, SO_2 (commonly called in everyday life by the older nomenclature of sulphurous acid), is a colourless, non-inflammable gas, with a suffocating odour (like burning sulphur). It dissolves freely in water. The solution has the odour of the gas, turns litmus paper red, and bleaches Brazil wood paper.[2] It contains sulphur dioxide (SO_2), sulphurous acid (H_2SO_3), and their ions. It gradually absorbs oxygen from the air, and is converted into dilute sulphuric acid. Sulphurous acid is an acid of medium strength: dissociation constants for the first stage $1.7 \cdot 10^{-2}$, for the second stage $5 \cdot 10^{-6}$.

2. The *salts* (sulphites) are colourless. Of the neutral salts only those of the alkali metals are easily soluble in water; of those which are insoluble or dissolve with difficulty, many dissolve in water containing free sulphurous acid as hydrogen sulphites (bisulphites), which are precipitated again on boiling.

3. When treated with sulphuric acid, all the salts develop sulphur dioxide, which can easily be distilled from their solutions. It may be recognised by the odour of such an acid solution, and detected in the air above such a solution by means of suitable reagents (see 9). (Method of detecting sulphite ion in the presence of sulphate ion.)

4. *Chlorine water* converts the sulphites into sulphates, and consequently dissolves most of them.

5. *Barium chloride precipitates the neutral salts*, but *not* the *free* acid. The precipitate dissolves in hydrochloric acid. *Alkali hydrogen sulphites yield sulphurous acid*, which remains *free* in solution, and *barium sulphite*, which is precipitated. *Strontium chloride*, like barium chloride, precipitates strontium sulphite. (Distinction from thiosulphate ion, Autenrieth and Windaus, *Zeitsch. anal. Chem.*, **37**, 290.)

6. *Hydrogen sulphide decomposes the free acid*, with the formation of water, pentathionic acid, $H_2S_5O_6$, and *free sulphur, which separates.*

7. If a piece of bright *copper wire* is introduced into a solution containing sulphur dioxide, to which an equal volume of *hydrochloric acid* has been added, and is then heated to boiling point, it appears black (as though coated with soot) in the presence of large quantities of sulphur dioxide, but dull and lustreless in that of small quantities (H. Reinsch).

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[1] In accordance with the nomenclature adhered to in this book, we call the acid sulphite salts with the anion HSO'_3 "hydrogen sulphite." The term "hydrosulphite," moreover, is also applied to the salts of the "hydrosulphurous acids" (Schutzenberger's), $H_2S_2O_4$, which are produced by the action of zinc on aqueous solutions of sulphur dioxide, and there are thus neutral, $Na_2S_2O_4$, and acid, $NaHS_2O_4$, hydrosulphites of this type. In all cases where it is a question of *these* hydrosulphites, we have called special attention to the fact by quoting the formula.

[2] See footnote, p. 431.

8. If hydrogen is evolved from zinc (free from sulphur) or aluminium and hydrochloric acid (free from sulphur dioxide) and a trace of sulphur dioxide or sulphite introduced into the flask, hydrogen sulphide is evolved with the hydrogen; the gas, therefore, *produces a black coloration and a precipitate in a lead acetate solution* treated with sodium hydroxide until the precipitate is re-dissolved.

9. *Sulphur dioxide is a powerful reducing agent*; it reduces chromates, permanganates, iodates, mercuric nitrate, and on heating (and in the absence of large quantities of alkali chlorides) mercuric chloride (to mercurous chloride),[1] decolorises iodine starch, gives a blue precipitate with a mixture of potassium ferricyanide and ferric chloride, etc. If filter paper, therefore, is saturated with a dilute *solution of starch*[2] containing a little pure *potassium iodate* (A. Franck), or with a solution of *ferric chloride* and *potassium ferricyanide* (C. Brown) and then dried, a very sensitive reagent paper is obtained. The blue colorations which appear are only distinctive of sulphur dioxide or sulphite when it is certain that no other reducing substances are present. The papers are therefore particularly suitable, when moistened, for the detection of small quantities of *gaseous sulphur dioxide*.

10. *Silver nitrate* precipitates *white silver sulphite* Ag_2SO_3 from a solution containing sulphite ion; it is soluble in nitric acid, ammonia solution and also in excess of sodium sulphite solution, with the formation of sodium - silver sulphite. The latter solution, as also the precipitate suspended in water, is decomposed on boiling, with the separation of silver, the liberation of sulphur dioxide and the formation of sodium— or silver sulphate.

11. A *hydrochloric acid stannous chloride solution* produces after a short time a *yellow precipitate of stannic sulphide*.[3]

12. If an aqueous alkali sulphite solution (if necessary after exact neutralisation with acetic acid, or after the addition of sodium hydrogen carbonate[4] until no longer acid) is added to a relatively large quantity of *zinc sulphate solution*, mixed with very little *sodium nitroprusside*, a red coloration will appear if the quantity of the sulphite is not too small; if, on the other hand, the quantity is very small, there is no coloration, but this is immediately produced if a solution of *potassium ferrocyanide* is added. In the case of not too small quantities, the addition of potassium ferrocyanide produces a purple-red precipitate (Bodecker). Alkali thiosulphates do not give the reaction, but their presence influences its sensitiveness (Autenrieth and Windaus, *Zeitsch. anal. Chem.*, **37**, 290).

13. *Neutral sulphites* (not hydrogen sulphites or free sulphur dioxide,

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[1] All these reduction reactions are only distinctive for sulphurous acid in the absence of other reducing substances. In particular the presence of the ions of trivalent antimony or divalent tin may lead to errors in the case of the mercuric reactions (Bollenbach, *Zeitsch. anal. Chem.*, **47**, 692).

[2] 2 grms. wheat starch, 100 grms. water and 0·2 grm. potassium iodate.

[3] *Cf.* Sec. 87, 5.

[4] An excess of sodium hydrogen carbonate does not matter. On the other hand, the presence of sodium carbonate or sodium hydroxide prevents a reaction.

which must first be neutralised by sodium hydrogen carbonate) *decolorise, almost immediately, dilute solutions of dyestuffs of the triphenylmethane series (magenta or malachite green).* *Acetaldehyde* in aqueous solution *reproduces the coloration*, owing to the formation of aldehyde sulphurous acid. Free alkali must be neutralised with carbon dioxide before it is added to the dyestuff solution. Thiosulphates, di-, tri-, and tetrathionates do not produce this reaction. On the other hand, it is produced by sulphides (not hydrogen sulphides). These must therefore be removed by means of zinc or cadmium salts (Votoček, *Ber.*, **40**, 414).

14. Sulphites, like sulphates, are *reduced to sulphides by heating with sodium carbonate on charcoal in the blowpipe flame.* (See Sec. 105, 9.)

15. With regard to the micro-chemical detection of sulphurous acid, *cf.* Denigès (*Pharm. Zentralhalle*, **33**, 98 (1892)).

SEC. 103.

2. Thiosulphuric acid, hyposulphurous acid, $H_2S_2O_3$ (Thiosulphate ion, $S_2O''_3$).

1. *Thiosulphuric acid* does not exist in the free condition. Its solutions decompose with the separation of *yellow* sulphur and the formation of sulphurous acid The *salts* of thiosulphuric acid, the thiosulphates (hyposulphites) are for the greater part soluble in water; the insoluble salts often form soluble double salts with sodium thiosulphate. Precipitates obtained by means of sodium thiosulphate often become soluble again, therefore, in an excess of the precipitant. The solutions of most thiosulphates may be boiled without decomposition (or they only decompose after being boiled for some time); calcium thiosulphate is decomposed, on boiling, into calcium sulphite and sulphur. The thiosulphates of heavy metals often form metal sulphides on boiling. Alkali thiosulphates decompose, when heated in the absence of air, into water, sulphur and hydrogen sulphide, which escape, and into a mixture of sulphide and sulphate, which remain.

2. If *sulphuric acid* or *hydrochloric acid* is added to a solution of thiosulphate, the liquid at first remains clear and odourless, but soon (the more concentrated and warm the solution is, the sooner this will take place) becomes more and more *turbid, owing to the sulphur which is separating,* whilst at the same time the *odour of sulphur dioxide* becomes noticeable.

3. *Silver nitrate* produces a *white precipitate of silver thiosulphate*, $Ag_2S_2O_3$, which is soluble in an excess of the thiosulphate solution, and after a while (at once, if heated) *becomes black* (distinction from sulphite ion. Bodnár, *Zeitsch. anal. Chem.*, **53**, 37), whilst the precipitate decomposes into *silver sulphide* and sulphuric acid.[1] Sodium thiosulphate solution dissolves silver chloride. On the addition of an acid, the solution at

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[1] With regard to its behaviour towards the solutions of other heavy metals, reference should be made to the sections dealing with the reactions of cations, as also to Part II., Chaps. III., IV.

first remains clear, but later (immediately, if heated) silver sulphide separates.

4. *Barium chloride produces a white precipitate*, soluble in large quantities of water (especially hot water), which is decomposed by hydrochloric acid.

5. *Strontium chloride* does *not* precipitate thiosulphates. (Distinction from sulphites.)

6. *Ferric chloride* gives a *reddish-violet coloration* to solutions of alkali thiosulphates. (Distinction from alkali sulphites.) The colour disappears on standing (rapidly, when heated), with the reduction of the ferric ion to ferrous ion.

7. *Acidified chromate solution* is *reduced* at once by thiosulphates to a *green chromic salt solution* ; chromate solutions, if *not acidified, turn brown*, and when heated yield a *brown* precipitate (*cf.* Sec. 101, 4).

8. *A solution of iodine and starch* and an *acidified* solution of *potassium permanganate* are immediately *decolorised.*

9. *Chlorine* and *bromine* oxidise thiosulphate ion to *sulphate ion* , iodine also oxidises thiosulphate ion to sulphate ion in alkaline solution. On the other hand, in acid solutions or those containing alkali hydrogen carbonate, it oxidises it to *tetrathionate ion.* Consequently thiosulphate solutions oxidised by chlorine and bromine, but not by iodine in the presence of acid or alkali hydrogen carbonate (distinction from sulphites), yield precipitates with barium chloride in acid solution. The oxidation to tetrathionate ion takes place without the formation of free acid :

$$2S_2O''_3 + I_2 = S_4O''_6 + 2I'$$

for example,

$$2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$$

(Distinction from sulphites, in the oxidation of which free acid is formed :

$$SO''_3 + H_2O + I_2 = SO''_4 + 2(H^{\cdot} + I')$$

for example,

$$Na_2SO_3 + H_2O + I_2 = Na_2SO_4 + 2HI$$

10. Thiosulphates behave towards *zinc* or *aluminium* and *hydrochloric acid* like the sulphites. If treated with potassium or sodium hydroxide and aluminium, thiosulphates yield sulphides of the alkali metals (de Koninck). (Distinction from sulphites.) Sodium amalgam reduces thiosulphates to sulphides. (Distinction from sulphites. Arnold and Mentzel, *Zeitsch. Untersuch. Nahr.*, **6**, 550.) On heating sodium thiosulphate solution with finely divided metals, metal sulphides and sodium sulphite are formed (F. Faktor, *Chem. Zentr.*, 1905, I., 1524).

11. If thiosulphate is heated with potassium cyanide, sulphite ion and thiocyanate ion are formed, $S_2O''_3 + CN' = SO''_3 + CNS'$ (Pechmann and Manck, *Ber.*, **28**, 2376). In solution, a conclusion can be drawn from the reaction of the thiocyanate with ferric chloride as to whether thiosulphate was originally present. (Distinction from sulphites. Gutmann, *Zeitsch. anal. Chem.*, **46**, 490.)

12. Thiosulphate solutions give an intense blue coloration with sodium nitroprusside solution, which has been exposed to air and light until it turns brown, or which has been treated with 1 or 2 drops of potassium

ferricyanide and 1 or 2 drops of sodium hydroxide solution, which coloration becomes considerably more intense on standing, on heating, and on the addition of a little potassium ferrocyanide. (Distinction from sulphites and tetrathionates. Casolari, *Chem. Zentr.*, 1911, I., 727.)

13. A solution of thiosulphate mixed with an equal volume of 10 per cent. ammonium molybdate solution and treated with concentrated sulphuric acid in such a way, that the liquids do not mix, shows a blue ring at the point of contact. (This is a very sensitive reaction, but is only distinctive in the absence of other reducing substances Pozzi Escot, *Chem. Zentr.*, 1913, II, 83)

14. With regard to the *microchemical detection* of thiosulphuric acid, see Huyse, *Zeitsch. anal. Chem*, **39**, 11.

If alkali sulphites and thiosulphates are to be detected in the presence of alkali sulphide, as is often the case, zinc sulphate solution is first added to the solution until the sulphide is decomposed; the zinc sulphide is then filtered off, and part of the filtrate tested for thiosulphate ion by the addition of hydrochloric acid, or with aluminum to which potassium hydroxide has been added; another part of the filtrate is tested for sulphite ion with sodium nitroprusside, etc., or, better (as the latter reaction is influenced by the presence of thiosulphates), with strontium chloride. For other methods of detecting sulphates, sulphides, sulphites and thiosulphates in the presence of each other, see *Zeitsch anal. Chem.*, **39**, 461; *ibid.*, **46**, 190, and **48**, 31, and also Feld, *Chem. Zentr*, 1898, II, 870; Weston, *ibid.*, 1910, I, 379.

SEC. 104.

3. Iodic acid, HIO_3 (Iodate ion, IO'_3).

1. *Iodic acid* forms colourless, rhombic crystals, and its *anhydride*, I_2O_5, is a crystalline, white powder. Both dissolve readily in water, and at a moderate heat decompose into iodine vapour, oxygen and, in the case of the acid, water. Iodic acid is a very strong acid, and is considerably dissociated in aqueous solution. With regard to the dissociation constants, K 0·19 at 15°, *cf.* the remarks in Abegg's *Handbuch*, **4**. 2, 503.

2. The *salts* iodates are decomposed on ignition either into oxygen and iodide, or into iodine, oxygen and metallic oxide; only the alkali iodates are easily soluble in water.

3. *Barium chloride* precipitates *white barium iodate*, $Ba(IO_3)_2$ (soluble in nitric acid), from solutions of alkali iodates.

4. *Silver nitrate* precipitates *white* granular-crystalline *silver iodate*, $AgIO_3$, which dissolves readily in ammonia solution, but only to a slight degree in nitric acid.

5. *Lead acetate* precipitates *white lead iodate*, $Pb(IO_3)_2$, which is scarcely soluble in water, and dissolves with difficulty in nitric acid.

6. *Hydrogen sulphide* precipitates *iodine* from a solution of iodic acid *with the simultaneous separation of sulphur*; the iodine then dissolves in the

hydriodic acid formed on the addition of more hydrogen sulphide. The liquid is decolorised on the addition of hydrogen sulphide in excess, with the further separation of sulphur, whilst the iodine is *completely* converted into iodine ion. Iodates are also decomposed by hydrogen sulphide.

7. *Sulphur dioxide* precipitates *iodine*, which is converted into iodine ion in the presence of an excess of sulphur dioxide.

8. A boiling saturated solution of *oxalic acid expels all iodine* from iodates.

9. *Phosphorus*, both colourless and red (the latter being particularly active), *reduces* iodic acid and iodates, even in very dilute solutions, with the formation of phosphate ion and the *separation of iodine* (Polacci).

10. Many other *reducing agents* act in the same way as those already mentioned. Thus, *hydrazine salts* (not free hydrazine), *phosphorous* and *hypophosphorous acids* cause a separation of iodine, even in the cold (Distinction from bromates, which are only decomposed on heating, and from chlorates,[1] which are not reduced at all.) Vitali, *Chem. Zentr.*, 1899, I., 1083. To detect iodic acid in nitric acid, the latter is preferably diluted with about 2 volumes of water, a little carbon bisulphide or chloroform and a drop of an aqueous solution of sulphur dioxide added, and the whole shaken. If iodic acid is present, the carbon bisulphide or the chloroform will turn violet, owing to the liberated iodine being absorbed. An excess of sulphur dioxide must, of course, be avoided.

11. On the ignition of iodates on charcoal before the *blowpipe*, *explosive fusion* takes place.

Second Division.

Of the first group of inorganic acids.

Sec. 105.

Sulphuric acid, H_2SO_4 (Sulphate ion SO''_4 and Hydrogen sulphate ion, HSO'_4).

1. *Sulphuric acid* at the ordinary temperature is an oily, colourless liquid, which, on cooling, solidifies into hexagonal crystals. Commercial "concentrated sulphuric acid" (see pp 18 and 110) contains a little water, and therefore does not correspond exactly to the formula H_2SO_4. *Sulphuric anhydride* (sulphur trioxide), SO_3, consists generally of a feathery-crystalline, white mass, which fumes when exposed to the air. Both carbonise organic substances. They combine with water in all proportions, showing a considerable increase of temperature—the anhydride hisses. If, therefore, concentrated sulphuric acid is to be diluted, it must be *gradually* poured into the water, and *water must never be added to concentrated sulphuric*

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[1] According to Schlötter (*Zeitsch. anorg. Chem.*, **38**, 184), chlorates are reduced by hydrazine sulphate on continued boiling.

acid. Sulphuric acid is a very strong acid. Its dissociation takes place in two stages, corresponding to the processes: $H_2SO_4 \rightleftarrows H^{\cdot} + HSO_4$ and $HSO'_4 \rightleftarrows H^{\cdot} + SO_4''$. In more dilute solutions sulphuric acid is as greatly dissociated as other strong acids.

2. The neutral sulphuric acid salts, sulphates, are, with the exception of barium, strontium, calcium and lead sulphates, easily soluble in water. The basic sulphates of heavy metals, which are insoluble in water, all dissolve in hydrochloric acid or nitric acid. Sulphates are mostly colourless or white. The alkali sulphates and alkaline earth sulphates will resist moderate ignition, but are more or less easily decomposed at a very high temperature. Of the remaining sulphates, many remain undecomposed on moderate ignition, whereas this decomposes others.

3. **Barium chloride** produces in *solutions containing sulphate ion*, even when extremely dilute, *a finely pulverulent, heavy, white precipitate*[1] *of barium sulphate*, $BaSO_4$, scarcely soluble in dilute hydrochloric and nitric acids. It is only precipitated from very dilute liquids after long standing. Concentrated acids and concentrated solutions of many salts influence, and a certain excess of barium chloride increases, the sensitiveness of the reaction. (*Cf.* the notes at the end of this section.) Barium sulphate is soluble in concentrated sulphuric acid. It separates again on dilution with water.

4. *Strontium chloride* (or nitrate) yields a *white precipitate* of *strontium sulphate*, $SrSO_4$ (distinction from thiosulphate ion), which is somewhat more easily soluble in acids than is barium sulphate.

5. **Lead acetate** precipitates *lead sulphate*, $PbSO_4$, as a *heavy, white precipitate*, which scarcely dissolves in water or dilute sulphuric acid, still less in alcohol, dissolves with difficulty in dilute nitric acid, and is completely soluble in hot concentrated hydrochloric acid. It is dissolved by hot solutions of ammonium acetate or ammonium tartrate.

6. *Mercuric acetate* and *mercuric nitrate* yield a *yellow precipitate* of *basic mercuric sulphate* (turpeth mineral), $HgSO_4.2HgO$, in solutions containing sulphate ion. The reaction takes place immediately on boiling, but less rapidly when cold. Halogen salts have a disturbing influence, as the precipitate dissolves in solutions containing them. The treatment of insoluble sulphates with

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[1] A whole series of communications deal with the properties of the precipitate, its solubility under various conditions, the simultaneous removal of other salts on precipitation, etc., which will be discussed more fully in connection with quantitative analysis.

mercuric acetate or nitrate solutions also produces a yellow precipitate. The reaction is also suitable for microchemical detection. (Denigès, *Chem. Zentr.*, 1918, I., 771.)

7. *A solution of benzidine in weak hydrochloric acid produces in neutral and acid solutions of sulphates a crystalline, white precipitate of benzidine sulphate*, which is scarcely soluble in water. Acids, ferric salts, green chromic salts and chromate ion influence the reaction.[1] The reaction is sensitive, but only indicative of sulphate ion when other anions which are sparingly soluble and yield benzidine salts, *e.g.* those of hydrofluoric acid or silicohydrofluoric acid (Ehrenfeld, *Chem. Zeit.*, **29**, 422) are not present.

8. The sulphates of the alkaline earth metals, insoluble in water and acids, yield alkali sulphates and alkaline earth carbonates on fusion with alkali carbonates; on similar treatment lead sulphate yields lead oxide as well as alkali sulphate. On digestion or boiling with concentrated solutions of alkali carbonates, the sulphates of alkaline earth metals and of lead are converted into insoluble carbonate and soluble alkali sulphate. In the case of barium sulphate, however, repeated boiling with fresh solution is necessary for complete decomposition.

9. If *sulphates are fused* with **sodium carbonate** on charcoal in the *inner blowpipe flame*, or are heated on *charcoal sticks* (p. 88) in the lower reduction flame, the sulphate is reduced and sodium sulphide is formed, which can be recognised by the odour of hydrogen sulphide if the fused mass, together with the piece of charcoal into which it has penetrated, is moistened and a little acid added. If the moistening with water takes place on a bright silver surface (a polished coin), a black spot of silver sulphide immediately appears (which, however, is only distinctive in the absence of tellurium and selenium compounds). As the gas flame contains sulphur compounds, the fusion tests in question must be carried out with the aid of candles or oil lamps.

10. With regard to the *microchemical detection* of sulphate ion, see Haushofer, p. 115; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 168; Denigès, *Chem. Zentr.*, 1918, I., 771.

Notes.—Of almost all anions, sulphate ion is the easiest to recognise, owing to its characteristic and exceedingly sensitive reaction with barium salts. Care must be taken not to mistake precipitates of barium chloride, and especially of barium nitrate, which are produced when aqueous solutions of these salts are mixed with liquids containing much free hydrochloric acid or nitric acid, for barium sulphate. These precipitates (differing from barium sulphate in their crystalline character) disappear immediately on dilution of the acid liquid with water, and are therefore very easy to distinguish from barium sulphate.

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[1] *Cf.* v. Knorre, *Zeitsch. anal. Chem.*, **49**, 469.

The habit should be formed in testing for sulphate ion with barium chloride to dilute the liquid sufficiently; a little hydrochloric acid should also be added, as this counteracts the detrimental influence of many salts, *e.g.* alkali citrates, and when very small quantities of sulphuric acid are to be detected, the liquid should be allowed to stand for several hours in a moderately warm place, after the addition of a sufficient excess of barium chloride. The trace of barium sulphate which has formed will have subsided. If there is any doubt as to the nature of the precipitate formed by barium chloride in the presence of free hydrochloric acid, a test according to 9 will determine the point. If small quantities of sulphate ion are to be detected with barium chloride in liquids which contain much free hydrochloric acid or nitric acid, the greater part of the free acid should first be removed by evaporation or by neutralisation with an alkali hydroxide. Free sulphuric acid is detected in the presence of sulphates by reducing the liquid under examination with a little cane sugar, and drying it in a porcelain dish at 100°. If free sulphuric acid is present, there will be a black, or in the case of very small quantities, a blackish-green residue Other free acids do not decompose cane sugar in this way. The reaction can also be carried out by adding a very small quantity of cane sugar, about 0·2 to 0·3 per cent., to the liquid and then dipping a strip of filter paper, 30 to 40 cm. long, into it After 24 hours the strip of paper is dried and heated at 100°. If free sulphuric acid is present, the paper will have become brown to black at the upper edge of the moistened portion and often quite brittle (Nessler)

Appendix.

The reactions for sulphates are also obtained with solutions of **persulphates,** as these decompose in solution into sulphates, sulphuric acid and water. *Persulphuric acid* has the formula $H_2S_2O_8$, persulphate ion $S_2O''_8$.

Cold freshly prepared solutions of potassium or ammonium persulphate do not give an immediate precipitation with *barium chloride*, but *barium sulphate* is precipitated on standing for some time, and at once on boiling. Persulphates can be recognised as such by their oxidising action. Thus, persulphate *liberates iodine from neutral solutions of potassium iodide.* (Distinction from perborate and percarbonate, which only give the reaction on the addition of sulphuric acid.) *Manganous, nickelous,* and *cobaltous salts* cause direct precipitation of higher oxides; on the other hand, persulphates do not decolorise *permanganate solutions,* or only to a slight extent, and do *not* give the blue coloration with *potassium dichromate* and *ether.* (Distinction from perborate and percarbonate.) If a 0·5 per cent. alcoholic *solution of benzidine* is poured upon a solution containing persulphate ion, an *intense blue precipitate* is formed at the point of contact, and beneath it a brown zone. This is a very sensitive reaction. (Distinction from chlorates, perchlorates, iodates, nitrates, perborates, and percarbonates.) Periodates show only a brownish-red ring, and do not give a blue precipitate (Monnier, *Chem. Zentr.*, 1917, I., 691).

A 0·2 per cent. methylene blue solution gives a pinkish-violet precipitate with alkali persulphates (very sensitive reaction). (Distinction from perchlorates, which give a violet precipitate, and from chlorates, iodates and periodates. Monnier, *Chem. Zentr.*, 1917, I., 691. *Cf.* also W. Lenz and E. Richter, *Zeitsch. anal. Chem.*, **50,** 537; E. H. Riesenfeld and W. Mau, *Ber.*, **44,** 3589.)

Sec. 106.

Silicohydrofluoric acid, H_2SiF_6 (Silicofluoride ion, SiF''_6).

1. *Silicohydrofluoric acid* is only known in aqueous solution. The solution is a strongly acid liquid, which, when evaporated in platinum, volatilises completely as silicon fluoride and hydrogen fluoride. When it is evaporated in glass, the latter is corroded. The acid forms with bases water and silicofluorides, which are for the greater part soluble in water, turn litmus red, and, on ignition, decompose into metal fluoride and silicon fluoride. An excess of strong bases decomposes the silicohydrofluoric acid, with the formation of fluorides and silicic acid, or silicates. Silicohydrofluoric acid is considerably dissociated, according to the result of conductivity measurements, in aqueous solution, and is consequently a comparatively strong acid.

2. Silicohydrofluoric acid becomes crystalline by the action of *barium chloride.* (Sec. 34, 6.)

3. This is not the case with strontium chloride.

4. It yields a white precipitate on the addition of an excess of lead acetate.

5. *Potassium salts* precipitate transparent gelatinous *potassium silicofluoride,* K_2SiF_6.

6. *Thorium nitrate* produces a white precipitate.

7. An excess of *ammonia* precipitates *silicic acid*, with the formation of *ammonium fluoride* (citric acid influences or prevents such precipitation. Guerry and Toussaint, *Chem. Zentr.*, 1906, II., 1085).

8. If silicofluorides are heated with concentrated *sulphuric acid*, hydrogen fluoride and silicon fluoride escape, forming strong fumes in the air; if the test is made in a platinum vessel covered with glass, the glass is etched (Sec. 111, 6), and the residue contains the corresponding sulphates. The vapours, when in contact with water or ammonia, yield a deposit of silicic acid (Sec. 111, 7).

Third Division.

Of the first group of inorganic acids.

Sec. 107.

(a) **Phosphoric acid,** H_3PO_4 (Phosphate ion, PO''_4, monohydrogen phosphate ion, HPO''_4, dihydrogen phosphate ion, $H_2PO''_4$).

The ordinary so-called white *phosphorus* is a colourless, greasy-looking, transparent, solid substance of sp. gr. 1·83, which is insoluble in water, dissolves slightly in alcohol and ether, and easily in carbon bisulphide. Taken internally it is extremely poisonous; it melts at 44·3°, boils at 290°, but volatilises to a slight extent even on distillation with water. Phosphorus kept under water first becomes yellow, owing to the action of light, then red, and finally becomes covered with a white coating.

If phosphorus comes into contact with the air at the ordinary temperature, it emits a quite characteristic and very unpleasant odour, and forms strong fumes, which are luminous in the dark. These are formed by the oxidation of phosphorus vapour and consist of phosphorus pentoxide, phosphorus trioxide, and phosphorus vapour. If the air is moist, ozone, hydrogen peroxide and ammonium nitrite are simultaneously formed. Phosphorus is very inflammable, and burns with a luminous flame to phosphorus pentoxide, the greater part of which spreads in the air as a white cloud. By long exposure to the light, or more rapidly by continuous heating at 250° in a vacuum, phosphorus changes into the red, so-called amorphous phosphorus.

When in this condition, it does not change in the air, is not luminous, is far less inflammable, is not poisonous, has a sp. gr. of 2·1, and does not dissolve in carbon bisulphide.

Nitric acid and *aqua regia* dissolve white phosphorus comparatively easily on heating. The solutions at first contain ions of phosphoric acid as well as those of phosphorous acid. *Hydrochloric acid* does not dissolve phosphorus. On boiling it with *potassium or sodium hydroxide*, or with *milk of lime*, hypophosphites and phosphates are produced, whilst hydrogen phosphide, which ignites spontaneously, escapes. If a substance containing white phosphorus is placed at the bottom of a flask, and a strip of paper moistened with a solution of *silver nitrate* is hung in the body of the flask by means of a loosely-inserted cork, and then heated at 30° to 40°, the strip of paper will turn black, owing to the reducing action of the phosphorus vapours, even when the quantity of phosphorus is exceedingly small. On boiling the blackened part of the paper in water, after completion of the reaction, precipitating the undecomposed portion of the silver nitrate with hydrochloric acid, and then filtering the liquid and evaporating the filtrate as completely as possible on the water bath, phosphate ion will be detected in the residue by means of the reactions described below (J. Scherer). It should be noted that silver nitrate may be turned black also by hydrogen sulphide, formic acid, and volatile products of putrefaction, and that the detection of phosphate ion in the strip of paper is only of value if the paper and the filter used for filtering the silver chloride were free from phosphoric acid. Further particulars regarding the behaviour of phosphorus will be found in Chap. II., Sec. 207, where the detection of phosphorus in forensic-chemical cases is dealt with; in particular, the phenomena which appear on boiling the solutions with dilute sulphuric acid, and on introducing them into a hydrogen generating apparatus charged with zinc and dilute sulphuric acid are there discussed.

With regard to processes devised specially for the detection of white phosphorus in matches, *cf.* F. Schröder, *Arbeit. Kais. Gesundh. Amt.*, **44**, 1; *Chem. Zentr.*, 1913, I., 1540.

2. *Phosphorus pentoxide*, phosphoric anhydride, P_2O_5, in the anhydrous condition, is a white mass, like snow, which deliquesces rapidly in the air, hisses on contact with water, in which it is at first partly, and gradually completely soluble. Three phosphoric acids correspond to the pentoxide (and also three kinds of salts), namely, *orthophosphoric acid*, H_3PO_4 (ion, PO'''_4), *pyrophosphoric acid*, $H_4P_2O_7$ (ion, $P_2O''''_7$) and *metaphosphoric* acid $(HPO_3)_n$ (ion $(PO'_3)_n$). Since only orthophosphates are of common occurrence in nature and in analytical work, we describe these only in detail, and deal more briefly with pyrophosphoric acid and metaphosphoric acid in the appendix.

3. *Orthophosphoric acid*, H_3PO_4, consists of transparent crystals, which deliquesce rapidly in the air to a syrup-like, non-corrosive

solution. On heating, it is converted, according to the quantity of water expelled, into pyro- or metaphosphoric acid: $2H_3PO_4 = H_4P_2O_7 + H_2O$ and $H_3PO_4 = HPO_3 + H_2O$. On continuous heating in an open platinum basin, phosphoric acid volatilises (if it is pure) with difficulty, but completely, in the form of white vapours. Orthophosphoric acid is tribasic. It therefore forms three series of salts: neutral (normal, tertiary), mono-acid (monohydrogen phosphates, secondary), and di-acid (dihydrogen phosphates, primary). The dissociation $H_3PO_4 \rightleftarrows H^{\cdot} + H_2PO'_4$ corresponds to an acid of medium strength, the second $H^{\cdot}$ ion is scarcely dissociated, and the third is only split off in the case of a large excess of OH' ions. Hence, in every solution containing orthophosphoric acid the anions PO'''_4, HPO''_4, and $H_2PO'_4$ are in equilibrium, whereby the proportion of the quantity of the individual ions depends on the concentration of the $H^{\cdot}$ ions. The ion PO'''_4 is the weakest, and consequently the solubility of the neutral orthophosphates the smallest.

4. *Neutral orthophosphates* (apart from ammonium phosphate) are not decomposed on heating; acid salts and ammonium metal orthophosphates are converted into pyro- or metaphosphates, *e.g.* disodium hydrogen phosphate into sodium pyrophosphate; magnesium ammonium phosphate into magnesium pyrophosphate, $2Mg(NH_4)PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$; monosodium dihydrogen phosphate or sodium ammonium hydrogen phosphate into sodium metaphosphate, $Na(NH_4)HPO_4 = NaPO_3 + NH_3 + H_2O$. Of the neutral orthophosphates only those of the alkali metals are soluble in water. They undergo hydrolytic dissociation, and therefore have an alkaline reaction towards indicators.[1] If pyro- or metaphosphoric acid salts are fused with sodium carbonate, the mass invariably contains orthophosphates only.

5. **Barium chloride** produces in *aqueous solutions of neutral or mono-acid alkali phosphates* (dialkali monohydrogen phosphates), but not in the solution of the di-acid salts (monoalkali dihydrogen phosphates), a *white precipitate of barium hydrogen phosphate*, $BaHPO_4$, or *neutral barium phosphate*, $Ba_3(PO_4)_2$, which is soluble in hydrochloric and nitric acids, but dissolves with difficulty in ammonium chloride solution.

6. **Calcium sulphate,** as also **calcium chloride,** *produces in solutions*

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[1] Disodium hydrogen phosphate also undergoes hydrolytic dissociation. Its reaction is neutral towards phenolphthalein, slightly alkaline towards litmus, and strongly alkaline towards methyl-orange. Sodium dihydrogen phosphate has an acid reaction towards phenolphthalein and litmus, and a neutral reaction towards methyl-orange.

of neutral or mono-acid phosphates, but not in a solution of dihydrogen phosphates or of the free acid, a *white precipitate of neutral calcium phosphate,* $Ca_3(PO_4)_2$, or of *calcium hydrogen phosphate,* $CaHPO_4+2H_2O$, which is *easily dissolved by acids, even by acetic acid,* if it is still amorphous. Ammonium chloride will also dissolve it then.

7. **Magnesium chloride** or **magnesium sulphate** *produces in concentrated solutions of mono-acid alkali phosphates* (dialkali monohydrogen phosphates), often after a long time, a *white precipitate of magnesium hydrogen phosphate,* $MgHPO_4+7H_2O$; if the liquid is boiled, a precipitate is immediately formed of *neutral magnesium phosphate,* $Mg_3(PO_4)_2+7H_2O$. This latter is also formed on the addition of a magnesium salt to the solution of a neutral alkali phosphate. *If, however, to free phosphoric acid or to a solution containing an alkali phosphate there is added* **magnesium chloride** *solution or magnesium sulphate solution (to which so much* **ammonium chloride** *has been added, that on the addition of ammonia it remains clear), and then* **ammonia** *in excess,*[1] *there is formed, even in the case of considerable dilution, a white, crystalline precipitate of magnesium ammonium phosphate* $Mg(NH_4)PO_4+6H_2O$, *which rapidly subsides, and which is scarcely soluble in ammonia solution and only slightly in ammonium chloride solution,* but is easily dissolved by acids, even acetic acid. The precipitate often becomes visible only after some time, but stirring assists its separation (*vide supra,* Sec. 37, 8). The reaction is only distinctive when no arsenate ion is present (Sec. 90, 8).[2]

8. **Silver nitrate** *precipitates from the solutions of neutral and mono-acid alkali phosphates silver phosphate,* Ag_3PO_4, as a bright yellow precipitate, readily soluble in nitric acid and in ammonia solution. (Distinction from pyro- and metaphosphate ion.) If a neutral phosphate was contained in the solution, the liquid, in which the precipitate is suspended, will give a neutral reaction; if a mono-acid salt was in solution, the reaction will be acid, owing to the liberation of nitric acid.

$$(Na_2HPO_4+3AgNO_3=Ag_3PO_4+2NaNO_3+HNO_3)$$

9. If a considerable quantity of *sodium acetate* is first added to a phosphate solution which contains no, or very little, free acid, and then *a drop of* **ferric chloride** added, a *yellowish-white* flocculent, gelatinous precipitate of *ferric phosphate,* $FePO_4+2H_2O$, is formed.

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[1] This mixture of magnesium salt with ammonium chloride and ammonia is also often used as a ready-prepared reagent under the name of "magnesia mixture."

[2] Or the ions of selenious or tellurous acids (Sec. 95, 7 and 96, 9).

(An excess of ferric chloride must be avoided, because the precipitate is not insoluble in the red complex ferric acetate compound thus formed.) This reaction is important for the detection of phosphate ion in alkaline earth phosphates, but is only distinctive when no arsenate ion is present, as this behaves in a similar manner. If the phosphate ion is to be completely separated as ferric phosphate, sufficient ferric chloride should be added to turn the solution red; it should then be boiled (in which process all the ferric ion will be precipitated, partly as phosphate, partly as basic acetate), and filtered while hot. Alkaline earth chloride will now be contained in the filtrate. If, with the aid of this reaction, phosphate ion is to be detected in the presence of much ferric ion, the hydrochloric acid solution is boiled with *sodium sulphite* until decolorised (reduction of the ferric ion to ferrous ion), sodium carbonate added until the liquid is almost neutral, then sodium acetate, and, finally, a drop of ferric chloride solution. (This process is based on the fact that *ferrous acetate solution* does not dissolve ferric phosphate.)

10. If *a few c.c. of the solution* of **ammonium molybdate** in *nitric acid* (*cf.* p. 111, Sec. 25, (4)) are introduced into a test-tube, and a *small quantity* of a neutral or acid liquid containing orthophosphate ion added, *there will be formed at once, or after a very short time in the cold*, if the quantity of phosphate ion is fairly considerable, *a finely pulverulent, bright yellow precipitate of ammonium* phosphomolybdate, $(NH_4)_3PO_4(MoO_3)_{12}+xH_2O$, which deposits on the sides and bottom of the tube. In the case of exceedingly small quantities of phosphoric acid, *e.g.* 0·00002 grm., several hours must be allowed for the reaction, and the solution slightly heated, but not above 40°. The liquid over the precipitate appears colourless (in the absence of other colouring substances) after complete separation of the precipitate. The above-mentioned yellow precipitate is only insoluble in dilute acids in the presence of an excess of molybdic acid; it should be noted that it is not formed by the addition of an excess of phosphate. Not more of the solution which is to be tested for phosphoric acid should, therefore, be used than is equal to a third of the molybdate solution, and a mere yellow coloration of the liquid should not be taken as a reaction for phosphate ion. Hydrochloric acid, when present in considerable quantity, influences or prevents the reaction. It can easily be removed by evaporation with nitric acid; certain organic substances, such as tartaric acid and reducing substances, also have a disturbing effect on the reaction, and should, therefore, if necessary, be removed by fusion with sodium carbonate and potassium nitrate.

The precipitate can, after settling, be easily recognised, even in dark-coloured liquids. If it is washed with the molybdate solution used for the precipitation, dissolved in ammonia solution, and magnesia mixture added (p. 414, footnote 1), magnesium ammonium phosphate is obtained.

By adopting the above-mentioned procedure, phosphate ion cannot well be mistaken for any other ion, for arsenate ion gives no precipitate with the molybdate solution in the cold, but if the liquid is heated, and especially if boiled, a precipitate is formed (the liquid above it appearing yellow after some time); silicate ion, however, gives no reaction at all in the cold, but on heating the liquid a strong yellow coloration is produced, but no precipitate.

11. If *metallic tin* (tin foil) is added to a strong nitric acid phosphate solution, *the whole phosphate ion separates, together with metastannic acid*, as stannic phosphate, insoluble in nitric acid (Method for separating phosphate ion from metal ions. Reynoso.)

According to Werner Mecklenburg,[1] it is, in the case of this precipitation, a question, not of a chemical compound, but of adsorption. It is, therefore, possible to produce the precipitation by the addition of colloidal ready-formed stannic hydroxide, instead of causing stannic hydroxide to be formed first from tin and nitric acid. Here, as in the precipitation with metallic tin, the liquid must not contain any appreciable quantity of hydrochloric acid. According to Gattermann and Schindhelm,[2] phosphate ion can be removed, even in the presence of hydrochloric acid with comparatively small quantities of tin, by precipitating the weak hydrochloric acid solution, heated to boiling point, with a concentrated stannic chloride solution, freshly prepared in the cold (0·5 grm. phosphoric acid to 2 to 3 grms. stannic chloride).

Small quantities of phosphate ion produce a precipitate, which is not very suitable for filtration. If the phosphate ions are to be removed, 0·3 grm. of diammonium hydrogen phosphate should be added to the solution before precipitation takes place.

12. If a finely ground substance containing a phosphate (or a metallic phosphide) is fused with 5 parts of a flux consisting of 3 parts of *sodium carbonate*, 1 part of *potassium nitrate*, and 1 part of *silicon dioxide*, in a platinum spoon or crucible, after the substances have been thoroughly mixed with one another, the mixture boiled with water, the solution poured off, *ammonium carbonate* added, this

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[1] *Zeitsch. anal. Chem.*, **52**, 293.

[2] *Ber.*, **49**, 2416; *Zeitsch. anal. Chem.*, **56**, 205.

boiled again, and the silicic acid thus precipitated filtered, alkali phosphate will be present in the solution, and phosphate ion may be detected in it according to 7, 8, 9, or 10.

13. On introducing a substance containing phosphate ion, which has been ignited and powdered, into a small glass tube, drawn out to a narrow diameter and closed at the bottom by fusion, and adding a piece of *magnesium wire* 4 mm. long (or a fragment of sodium), which must be covered by the substance under examination, and then heating the mixture, *magnesium* (or sodium) *phosphide* is formed with bright incandescence, and the compressed black mass consequently emits the characteristic odour of *hydrogen phosphide* when moistened with water (Winkelblech, Bunsen).

14. *Albumin* is precipitated neither by a solution of orthophosphoric acid, nor by a solution of orthophosphates, treated with acetic acid.

15. With regard to the *microchemical detection* of phosphate ion, see Haushofer, *Mikroskopische Reaktionen*, p 108; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 198

SEC. 108.

Appendix.

(*a*) **Pyrophosphoric acid,** $H_4P_2O_7$ (Pyrophosphate ion, $P_2O''''_7$).

1. A solution of *pyrophosphoric acid,* when boiled, is converted into one of orthophosphoric acid. The solutions of the salts may be heated without undergoing decomposition, but if they are boiled with strong acids, the pyrophosphate ion is converted into orthophosphate ion. By fusing the salts with sodium carbonate in excess, orthophosphates are obtained. Pyrophosphoric acid forms only two series of salts, neutral with the anion $P_2O''''_7$, and acid with the anion $H_2P_2O''_7$. Of the neutral pyrophosphates, only those of the alkalis are soluble in water; the acid salts, *e g.* $Na_2H_2P_2O_7$, are converted on ignition, with the separation of water, into metaphosphates, $NaPO_3$.

2. *Barium chloride* does not precipitate the free acid, but gives a white precipitate of *barium pyrophosphate*, $Ba_2P_2O_7$, soluble in hydrochloric acid, with solutions of the salts.

3. *Silver nitrate* precipitates from a solution of pyrophosphoric acid, especially on the addition of an alkali, *silver pyrophosphate*, $Ag_4P_2O_7$, as a *white* (distinction from orthophosphate ion), earthy precipitate, soluble in nitric acid and ammonia solution.

4. *Cupric sulphate* produces in an acetic acid solution of pyrophosphates a bluish-white precipitate.

5. *Cadmium chloride* gives in acetic acid solution a white precipitate, insoluble in an excess of the precipitant. (Ortho- and metaphosphates

are not precipitated by cupric and cadmium salts under these conditions. C. Arnold and G. Werner.)

6. *Magnesium sulphate* precipitates *magnesium pyrophosphate*, $Mg_2P_2O_7$. The precipitate dissolves on the addition of an excess of pyrophosphate or of magnesium salt. It is not precipitated from these solutions by ammonia. (Distinction from metaphosphate ion.) When the solutions are boiled, however, it separates.

7. If *hexamine-cobaltitrichloride* (luteo-cobalt chloride), $[Co(NH_3)_6]Cl_3$, is added to a not too dilute solution of an alkali pyrophosphate, a pale reddish-yellow precipitate, consisting of lustrous crystalline flakes, is at once obtained. The precipitation does not take place in acetic acid solution. (Distinction from ortho- and metaphosphate ion. C. D. Braun.)

8. *Albumin* is not precipitated, either by a solution of pyrophosphoric acid or by a solution of the salts, treated with acetic acid.

9. *Ammonium molybdate*, with the addition of nitric acid, at first produces no precipitate, but later, yellow ammonium phosphomolybdate separates from the liquid in the proportion in which the pyrophosphate ion is converted into orthophosphate ion.

(β) **Metaphosphoric acid,** $(HPO_3)_n$ (Metaphosphate ion, $(PO_3)'_n$).

1. A whole series of different, mainly polymeric, compounds, corresponding to the formula $(HPO_3)_n$, is termed *metaphosphoric acid*. Up to the present the constitution of eight kinds of metaphosphates have been definitely determined, and the acids corresponding to them have, for the greater part, been prepared. The reactions which distinguish the individual metaphosphates are not mentioned here, and we confine ourselves to the remark that the metaphosphoric acids differ from the ortho- and pyrophosphoric acids in that the solutions of metaphosphoric acids at once precipitate *albumin*, whilst the solutions of the salts only precipitate it on the addition of acetic acid.

2. A white precipitate is formed by those metaphosphoric acids and salts which are precipitated by *silver nitrate*.

3. *Magnesium sulphate* produces no precipitate, but does so on the addition of ammonia. The precipitate dissolves in an excess of ammonium chloride solution.

4. *Hexamine-cobaltitrichloride* produces in an aqueous solution of metaphosphates a brownish-yellow precipitate; the precipitation takes place also in acetic acid solution. (Method of detecting metaphosphates in the presence of the two other phosphates. C. Arnold and G. Werner.)

5. All metaphosphates, when fused with *sodium carbonate* in excess, yield sodium orthophosphate.

SEC. 109.

(b) **Boric acid,** H_3BO_3 (Metaborate ion, BO'_2).

1. *Crystallised boric acid* (*orthoboric acid*), H_3BO_3, consists of scaly flakes, soluble in water and alcohol. On evaporating the solutions, a large quantity of boric acid volatilises with the water

or alcohol vapours. The solutions turn litmus red and give a *pale (when dried, dark) brownish-red coloration to* **turmeric paper.** When heated at 100°, boric acid loses one molecule of water, and is converted into *metaboric acid*, HBO_2; at 140° *tetraboric acid* is formed, $H_2B_4O_7$. Other "condensed" boric acids are also known, which, like the above-mentioned, are all formed by water being eliminated from orthoboric acid and the residual molecules combining to form larger complexes. On ignition, *boric anhydride* (boric trioxide), B_2O_3, is formed as a fusible hygroscopic glass, which resists the action of heat. The *salts* of boric acid (borates) are mainly derived from meta- and tetraboric acid (borax, $Na_2B_4O_7.10H_2O$), and are not decomposed on ignition; only the alkali borates are easily soluble in water; their solutions are colourless and, owing to hydrolysis, show an alkaline reaction. In dilute aqueous solutions borax is completely decomposed by the absorption of water into free boric acid and a borate—either NaH_2BO_3 or $NaBO_2$, probably the latter. The process would thus be: $Na_2B_1O_7+3H_2O=2Na^{\cdot}+2BO'_2+2H_3BO_3$ (Shelton, *Zeitsch. physik. Chem.*, **43**, 494). Boric acid is a very weak acid, with the dissociation constant $K=1.7.10^{-9}$ at 18°, or $2.3.10^{-9}$ at 25° for the process

$$H_3BO_3\rightleftarrows H^{\cdot}+H_2BO'_3,\ \text{or}\ HBO_2\rightleftarrows H^{\cdot}+BO'_2$$

2. **Barium chloride** produces in *not too dilute solutions* of alkali borates a *white precipitate*, soluble in acids and solutions of ammonium salts, of *barium borate*, the formula of which, on the precipitation of metaborates, is $BaB_2O_4+2H_2O$; on the precipitation of tetraborates the combination of the precipitate is given as $Ba_3B_{10}O_{18}+6H_2O$ (H. Rose), but this depends on the conditions.

3. **Silver nitrate,** mixed with *concentrated solutions* of alkali *metaborates*, yields a *white* (slightly yellowish, owing to the presence of free silver oxide) *precipitate*, $2AgBO_2+H_2O$, whilst from concentrated solutions of *tetra*borates it gives a *white precipitate*, the composition of which is said to correspond to the formula $Ag_6B_8O_{15}$. *Dilute* solutions of alkali borates give with silver nitrate a *brown precipitate* of silver oxide, and under certain conditions alkali tetraborates also yield silver metaborate, $AgBO_2$ (H. Rose). All these precipitates dissolve in nitric acid and in ammonia solution.

4. On the addition of **dilute sulphuric acid** or **hydrochloric acid** to *very concentrated* solutions of alkali borates, *prepared with the aid of heat, boric acid separates*, on cooling, *as lustrous crystalline flakes.*

5. *On treating a solution of an alkali borate or an alkaline earth borate with* **hydrochloric acid** *until the reaction is distinctly acid, and*

dipping into it half of a **strip of turmeric paper,** *which is then dried on a watch-glass at 100°, the half originally moistened will show a characteristic red colour* (H. Rose). The colour does not disappear when the paper is dipped into dilute acids, as in the case of the reaction produced by alkaline liquids. *If the turmeric paper, coloured red by the boric acid, is moistened with a solution of an* **alkali hydroxide** (or ammonia), or **alkali carbonate,** *the colour changes to blue-black or green-black;* a little hydrochloric acid will, however, restore the brownish-red colour (A. Vogel, H. Ludwig).

This reaction is very sensitive. Care should be taken not to confuse the characteristic red coloration with the blackish-brown coloration which turmeric paper assumes when moistened with somewhat concentrated hydrochloric acid and then dried, or with the brownish-red coloration which ferric chloride, or a hydrochloric acid solution of molybdic, titanic, niobic, or tantalic acids or zirconia impart immediately (and to a greater degree on drying) to turmeric paper. The coloration produced by these substances does *not* change into bluish or greenish black when moistened with alkali hydroxide or alkali carbonate solutions. The turmeric reaction is particularly sharp when the borate solution, acidified with hydrochloric acid, is evaporated to dryness on the water bath, with the addition of 2 or 3 drops of turmeric solution or turmeric tincture. The residue has a brownish-red colour. The reaction is inhibited by the presence of chlorates, chromates, iodides and nitrites, which salts must, therefore, first be removed or destroyed.

6. *Free boric acid and volatile boric compounds* produce a *green coloration* in the non-luminous **gas-flame.** The coloration becomes visible when a borate, after being moistened with concentrated sulphuric acid, is heated on the lower edge of a Bunsen flame on a loop of platinum wire.

7. *When* **alcohol** *is poured over free boric acid or borates* (in the case of the latter **concentrated sulphuric acid** being added in order to liberate the boric acid), and *the alcohol ignited, the flame,* especially when the liquid is stirred, *will be coloured a distinct yellowish-green* by the burning *boric acid ethyl ester.* The reaction is most sensitive when the dish containing the mixture is heated, the alcohol ignited, allowed to burn for a short time, extinguished and then ignited again. When the alcohol first flares up the edges of the flame will appear green, even when the quantity of boric acid is so small that no flame coloration is visible by the use of the ordinary method. *Concentrated* sulphuric acid should be used, and *in not too small quantity.*

As copper salts also colour the spirit flame green, any copper present must be removed by means of hydrogen sulphide. The presence of chlorides may also lead to mistakes, as the resulting ethyl chloride colours the flame bluish-green.

The flame coloration of the methyl ester of boric acid is also very characteristic of boric acid. For the purpose of the reaction a short, wide, small test-tube, provided with a cork with two holes, should be used. A glass tube bent at right angles is inserted into each of the holes; one should reach nearly to the bottom of the test-tube, the other to only just below the cork. The projecting arm of the latter, about 5 cm. long, is constricted to about 1 mm. On introducing a small quantity of a substance containing boric acid into the test-tube, adding a little concentrated sulphuric acid and gradually, on cooling, a little methyl alcohol, conducting pure hydrogen through the small apparatus, and igniting it after the atmospheric air has been removed, it will burn with a green flame, owing to the presence of the methyl ester of boric acid, $B(OCH_3)_3$, and, when spectroscopically examined, the flame will show the characteristic boric acid spectrum (see 10, Rosenbladt). When using this reaction according to the methods of estimation used in the official examination of meat,[1] the substance to be examined is powdered (*i.e.* ash formed by ignition with alkali hydroxide) with a cold mixture of 5 c.c. of methyl alcohol and 0.5 c.c. concentrated sulphuric acid, is then placed in a small distillation apparatus with a further 5 c.c. of methyl alcohol, and the methyl alcohol completely distilled on the water bath after standing for half an hour. The distillate can then be tested for boric acid in an apparatus similar to that described above, through which dry hydrogen is passed, and by the use of a platinum wire. There is no possibility of confusion with barium and copper salts in this reaction. If, instead of being ignited, the gas, which escapes on distillation with methyl alcohol and sulphuric acid, is conducted through a little potassium hydroxide solution, free from silicates, this solution treated in a platinum basin with hydrofluoric acid, and evaporated to dryness on the water bath, *potassium borofluoride*, KBF_4, is formed, which remains undissolved when the residue is treated with a solution of 1 part of potassium acetate in 4 parts of water.

8. On mixing a finely-powdered substance containing boric acid, after the addition of a drop of water, with 3 parts of a *flux* consisting of 4½ parts of *potassium pyrosulphate* and 1 part of finely powdered *fluorspar*, free from boric acid, and introducing the mixture on a loop

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[1] *Zeitsch. anal. Chem.*, **47**, 18.

of platinum wire into the outer zone of a Bunsen flame or into the point of the *inner blowpipe flame*, *boron fluoride*, BF_3, *escapes and turns the flame green*, but only for a few moments (Turner). In the case of easily decomposed compounds the reaction may be produced by moistening the substance with silicohydrofluoric acid, and introducing it into the flame. The sensitiveness of the test may be increased by mixing the substance thoroughly with silicon dioxide and fluorspar, and heating the mixture in a test-tube, after adding a small piece of marble, with concentrated sulphuric acid, and allowing the escaping gases to penetrate into a non-luminous Bunsen flame through a glass tube, bent at right angles, attached to the point of a platinum blowpipe tube (Kämmerer). The reaction is specially suitable for the detection of boric acid in insoluble silicates containing boron.

9. On heating a dry substance containing boric acid with an equal or half its volume of *ammonium silicofluoride*[1] in a glass tube closed by fusion at the bottom, finally to ignition point, a sublimate of *ammonium borofluoride*, $(NH_4)BF_4$, is obtained, which, when introduced into the non-luminous flame, gives it a *green colour* and, when dissolved in water, gives the *turmeric reaction* mentioned in 5. If the substance under examination contains a free acid, it should be treated with a slight excess of sodium carbonate (Stolba).

10. By fusing boric acid or borates with sodium carbonate on a loop of platinum wire, and heating the bead in the flame of a **spectroscope,** the *spectrum* will be recognised (even in the case of small quantities of boric acid) as one containing 4 *pronounced bright lines* of equal breadth and at equal distances from one another. B_1 is yellowish-green and brilliant (according to the Table I., 63 to 66), B_2 is light green and brilliant (77 to 80), B_3 is pale bluish-green (89 to 92), and B_4 is very pale blue (104 to 105) (Simmler, M. W. Iles). Eder and Valenta put the maxima of the boric acid spectroscopic bands at the following wave lengths: 639·7, 620·8, 603·0 579·7, 547·8, 543·9, 517·2, 492·0, 470·9, 452·9 $\mu\mu$. Also when a finely-powdered substance containing boric acid is rubbed with *glycerin* to a thick paste and introduced on a loop of platinum wire into the flame of a Bunsen burner, a green flame is obtained, which is very suitable for spectroscopic examination (M. W. Iles).

11. For the *microchemical detection* of boric acid, see Haushofer, *Mikroskopische Reaktionen*, p. 30; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 103.

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[1] This can be obtained by careful neutralisation of silicohydrofluoric acid with ammonia and evaporation of the filtrate in a platinum basin.

Appendix.

As supplementary to the reactions of boric acid, **perboric acid,** HBO_3 (Perborate ion, BO'_3) may be mentioned. As perborates decompose more or less easily into hydrogen peroxide and metaborates, $NaBO_3+H_2O \rightleftarrows NaBO_2+H_2O_2$, they also give the borate ion reactions. The oxidising actions of perborate ion are characteristic of it. Thus, when treated with *potassium dichromate* and shaken with *ether*, it gives a blue coloration to the layer of ether.

Chrome alum, decomposed with perborate and shaken with ether also gives a blue coloration. (Distinction from percarbonates. Monnier, *Chem. Zentr.*, 1917, I., 691.)

Titanium trichloride produces a red coloration. *Cerous chloride* is coloured yellow.

A neutral, but not an acidified, *potassium permanganate solution* is decolorised, with the separation of manganese dioxide.

Neutral *manganous*, *nickelous* and *cobaltous salt solutions* give dark precipitates of the higher oxides.

Perborates only liberate iodine from *potassium iodide* after acidification.

Cf. also W. Lenz and E. Richter, *Zeitsch. anal. Chem.*, **50**, 537.

SEC. 110.

(c) Oxalic acid, $H_2C_2O_4$ (Oxalate ion, $C_2O''_4$).

1. *Anhydrous oxalic acid*, $H_2C_2O_4$, is a white powder; the crystallised oxalic acid, $H_2C_2O_4+2H_2O$, forms colourless, rhombic rods. Both compounds dissolve easily in water and alcohol. Heated quickly in open vessels, the anhydrous acid is partly decomposed, without the separation of carbon, and partly volatilised without decomposition. The vapours have a very irritating effect on the throat. If anhydrous acid is heated in a test-tube, it partly sublimes without decomposition. Oxalic acid and its salts are poisonous. Oxalic acid in aqueous solution is a moderately strong dibasic acid. The dissociation constant for the process $C_2O_4H_2 \rightleftarrows C_2O_4H'+H^{\cdot}$ is about 0.1.

2. As a dibasic acid, oxalic acid forms *neutral and acid salts* (*oxalates*), and also *tetraoxalates*, which are compounds of one molecule of an acid salt with one molecule of oxalic acid, *e.g.* $KHC_2O_4+H_2C_2O_4+2H_2O$.

The oxalates are all decomposed on ignition, the anion being decomposed into carbon dioxide and carbon monoxide. Thus, the oxalates of the alkali metals, as also of the alkaline earth metals (if they are pure and are slowly heated), are converted into carbonates (almost without separation of carbon); magnesium oxalate changes to magnesium oxide, even on very gentle ignition; the salts of heavy metals give a residue of metal or oxide, according to the reducibility of the metallic oxide. Of the salts of oxalic acid, the neutral oxalates of the alkali metals are soluble in water, the acid oxalates dissolve less readily; magnesium oxalate and a few oxalates of heavy metals are also soluble in water. The insoluble metal oxalates form with alkali oxalates soluble double salts.

3. **Barium chloride** *yields in neutral solutions of alkali oxalates a white precipitate of barium oxalate*, $BaC_2O_4+H_2O$ This is scarcely soluble in water, but dissolves more readily in ammonium chloride solution, water containing acetic acid or oxalic acid, and easily in nitric and hydrochloric acids; ammonia precipitates it from the last solutions unchanged.

4. **Lead acetate** produces in solutions of oxalic acid and of alkali oxalates a *white precipitate of lead oxalate*, PbC_2O_4, which is sparingly soluble in cold dilute nitric acid The washed precipitate does not dissolve in ammonia solution.

5. **Silver nitrate** produces in aqueous solutions of oxalic acid and of alkali oxalates a *white precipitate of silver oxalate*, $Ag_2C_2O_4$. It is only slightly soluble in water, dissolves with difficulty in dilute nitric acid, but easily in concentrated hot nitric acid, as also in ammonia solution. When rapidly heated, it fuses explosively.

6. **Manganous sulphate** and **manganous chloride** produce in solutions of oxalic acid and neutral alkali oxalates an *almost white, crystalline precipitate of manganous oxalate*, $MnC_2O_4+3H_2O$.

7. **Lime-water** and all *soluble calcium salts*, as also **calcium sulphate solution,** produce in aqueous solutions of oxalic acid and of alkali oxalates (even when extremely dilute) *white, pulverulent precipitates of calcium oxalate*, $CaC_2O_4+H_2O$, and occasionally $CaC_2O_4+3H_2O$, which are *practically insoluble in water, scarcely soluble in acetic acid and oxalic acid solution*, but dissolve easily in dilute hydrochloric and nitric acids. Ammonium salts in no way hinder its formation. The addition of ammonia has a considerable influence in promoting the precipitation of free oxalic acid by calcium salts. In very dilute solutions, the precipitation only takes place after some time, but more rapidly on heating.

8. *Potassium salts, e.g.* potassium chloride, and *acetic acid* produce in concentrated aqueous oxalate solutions a crystalline precipitate of *potassium hydrogen oxalate* or *tetraoxalate.* Its separation is promoted by the addition of alcohol. The precipitate dissolves readily in alkali hydroxide solutions and mineral acids. In the case of dilute solutions there is no precipitation.

9. *If oxalic acid or an oxalate in the dry condition is heated* with an excess of **concentrated sulphuric acid,** the oxalic acid is *decomposed,* with the separation of water, and *carbon dioxide* and *carbon monoxide* are formed, which escape with effervescence :

$$H_2C_2O_4 = H_2O + CO_2 + CO$$

If the test is made on not too small a scale, *the escaping carbon monoxide may be ignited ; it burns with a blue flame.* If the sulphuric acid becomes dark in the course of this reaction, the oxalic acid must have been mixed with an organic substance (in the analytical sense. *Cf.* Sec. 99, second paragraph).

10. On mixing oxalic acid or an oxalate with a little finely-powdered **manganese dioxide** (which must be free from carbonates), and adding a little water and a few drops of **concentrated sulphuric acid,** there will be a *vigorous effervescence produced by the escaping carbon dioxide,* $MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$. Free oxalic acid will show the reaction without the addition of sulphuric acid, but it will be less sensitive

11 On treating a solution of *ferrous phosphate* in phosphoric acid with an oxalate solution, the liquid will have a deep yellow colour. The sensitiveness of the reaction is increased by gentle heating (Gunn)

12. If solid oxalic acid or an oxalate is treated with a few drops of a solution of *resorcinol in concentrated sulphuric acid* (about 1 : 100), and carefully heated until sulphuric acid vapours begin to escape (about 130° to 140°), *the liquid will become deep blue.*

13. On dissolving a small crystal (3 to 5 mgrm) of *manganous sulphate* in a few drops of water, adding a drop of sodium hydroxide solution, heating the liquid and, when cooled, adding drop by drop the solution which is to be tested for oxalic acid or its salts (which must be free from reducing substances and, if necessary, slightly acidified with sulphuric acid) to the manganous manganic hydroxide (Sec. 58, 6), a red coloration will appear in the presence of oxalate ion, as soon as the precipitate has dissolved. This is a sensitive reaction, suitable for the detection of oxalic acid ions in the presence of the ions of hydrochloric, sulphuric, nitric, phosphoric, acetic,

butyric, valeric, citric, tartaric, lactic, benzoic and salicylic acids, and of phenol, and also of small quantities of formic acid (J. F. Sacher, *Chem. Zeit.*, **39,** 319; *Chem. Zentr.*, 1915, I., 1282).

14. When the oxalates of the alkaline earth metals are boiled with a concentrated solution of *sodium carbonate* and filtered, sodium oxalate will be found in the filtrate, and alkaline earth carbonate in the precipitate. So far as the oxalates of the heavy metals are concerned, it is not always possible to attain the object in view completely by the use of this process, as many of these oxalates are partially soluble in alkaline liquids with the formation of double salts, *e.g.* nickel oxalate. Such heavy metal cations must, therefore, be separated as sulphides.

15. With regard to the *microchemical detection* of oxalic acid or of calcium oxalate, *cf.* C. Bischoff, *Zeitsch. anal. Chem.*, **22,** 633; Haushofer, *Mikroskopische Reaktionen*, p. 81; Behrens, *Anleitung zur mikrochemischen Analyse*, 1st ed., vol. 1, p. 39.

SEC. 111.

(d) **Hydrofluoric acid,** HF (Fluorine ion, F′).

1. Anhydrous *hydrofluoric acid* is a colourless liquid, which gives off strong fumes in the air, boils at 19·4°, and is readily soluble in water. *Aqueous hydrofluoric acid* differs from all other acids in that it is capable of dissolving silicon dioxide, and also of dissolving or decomposing silicates insoluble in hydrochloric acid. In the solution of silicon dioxide, silicon hydrogen fluoride is produced, with the simultaneous formation of water: $SiO_2+6HF=H_2SiF_6+2H_2O$ In combination with metal oxides, hydrofluoric acid yields fluorides and water. Hydrofluoric acid produces blisters on the skin similar to the blister of a burn (often they do not appear for some time) therefore care is necessary in handling this acid. In dilute solutions, the behaviour of hydrofluoric acid is that of a somewhat weak monobasic acid. The dissociation constant for the process $HF \rightleftarrows H^{\cdot}+F'$ is, according to Pick, $7.2\ 10^{4}$ In concentrated solutions hydrofluoric acid is materially stronger, owing to the formation of hydrogen fluoride ions, corresponding to the equation $HF+F' \rightleftarrows HF'_2$. (*Cf.* Abegg, **4,** 2, p. 34 *et seq.*)

2. Of the *fluorides* those of the alkali metals are soluble in water, and their solutions give an alkaline reaction; those of the alkaline earth metals do not dissolve, or only with great difficulty, in water.

Anhydrous aluminium fluoride is not soluble; on the other hand, a modification of the heptahydrate $2AlF_3.7H_2O$ dissolves in water. Many of the fluorides of heavy metals dissolve with great difficulty in water, *e.g.* cupric, lead and zinc fluorides; others dissolve in water without difficulty, such as nickelous and cobaltous fluoride, silver antimony and stannic fluorides. Many of the fluorides which are insoluble in water, or only dissolve with difficulty, form with free hydrofluoric acid soluble hydrogen fluorides; the alkali fluorides also combine with hydrofluoric acid: the fluorides of most heavy metals unite with alkali fluorides to form double salts. Most fluorides do not undergo decomposition when ignited in a crucible; on being *evaporated* with *concentrated sulphuric acid* they are decomposed (whilst hydrofluoric acid escapes), and converted into sulphates.

3. **Silver nitrate** does *not* give a precipitate with solutions of hydrofluoric acid and fluorides.

4. **Barium chloride** precipitates fluorine from an aqueous solution of hydrofluoric acid, and more completely from solutions of alkali fluorides. The voluminous white precipitate, *barium fluoride*, BaF_2, is practically insoluble in water, but dissolves in fairly large quantities of hydrochloric or nitric acid; ammonia does not re-precipitate it, or only incompletely from these solutions, owing to the solvent action of ammonium salts.

5. By adding **calcium chloride** to an aqueous solution of hydrofluoric acid or of a fluoride, *calcium fluoride*, CaF_2, is obtained in the form of a gelatinous precipitate, which is so transparent that at first one is apt to assume that the liquid has remained clear. The addition of ammonia promotes a complete separation of the precipitate. This is practically insoluble in water and scarcely soluble in hydrochloric and nitric acids in the cold, but dissolves more readily when boiled with hydrochloric acid. Ammonia does not produce a precipitate, or only a slight one, in this solution, because the ammonium salt which has been formed keeps it in solution. Calcium fluoride is hardly more soluble in free hydrofluoric acid than in water; it is insoluble in alkaline liquids.

6. When a finely powdered fluoride (it is immaterial whether it is soluble or insoluble) is treated in a *platinum crucible* with just sufficient **concentrated sulphuric acid** to form a thin paste, the crucible covered with a *clock glass* of hard glass, the convex side of which is covered with a *layer of wax*, on which *marks have been* drawn with a fine wooden point, the hollow of the clock glass filled with water or ice and *the crucible placed on a warm plate, the marks*

will be found after half an hour or an hour to be more or less *etched*, which can be clearly seen when the wax has been removed. (To replace the layer of wax, the clock glass should be carefully heated, a piece of wax laid on it, and, as it melts, evenly spread over it; to remove it, the glass should again be gently heated and the wax wiped off with a cloth.) If the quantity of hydrofluoric acid liberated by the sulphuric acid is very small, it often happens when the wax is removed that the marks are no longer to be seen, but by breathing on the glass the marks become visible again, owing to the unequal capacity of the etched parts of the glass and those not attacked to condense water. As, however, such markings developed by breathing may be due to other causes, the conclusion may be drawn from the fact that they do not appear, that fluorine ion was absent, but the appearance of these markings is not necessarily conclusive that it was present. In any case, they should not be considered decisive, unless they can be reproduced after the clock glass has been thoroughly cleaned and rinsed with water, dried and wiped.[1]

The reaction mentioned is not successful in the presence of too much silicic acid, or when the substance cannot be decomposed by sulphuric acid. In such cases one of the two following methods should be used:—

7. *On heating a finely-powdered substance, decomposable by concentrated sulphuric acid and containing fluoride* (by itself, if it contains much silicic acid,[2] or *after the addition of finely-powdered* **quartz,** if it contains little or no silicic acid), *with* **concentrated sulphuric acid,** *silicon fluoride*, SiF_4, *escapes, which forms thick white fumes in moist air, and gives a deposit of silicic acid*, $Si(OH)_4$, *when brought into contact with water or ammonia.* If the gas is introduced into *water* by means of a glass tube moistened on the inside, the tube becomes *opaque* from the separation of silicic acid; when present in larger quantity, *silicic acid also separates* in the water, while the liquid is rendered acid by *silicohydrofluoric acid*,

$$3SiF_4+4H_2O=Si(OH)_4+2H_2SiF_6$$

For the purpose of detecting small quantities of fluorine by this method, the substance is heated with concentrated sulphuric acid at about 160 in a small flask with a cork, through which two tubes are passed. A slow current of dry air is introduced through the one tube (which should reach to the bottom of the flask), and expelled by the short tube (which should terminate below the cork), and through a **U**-shaped tube, which has a bulb at the base containing a drop of water, and the other end of which is connected with an aspirator. The silicon fluoride which escapes with the air deposits (at the place where it comes into contact with the water) *silicic acid*, even very small quantities of which may be easily recognised by means of the above-mentioned arrangement of the apparatus. *Potassium hydrogen sulphate* is used in the case of substances, which do not decompose readily, in the place of sulphuric acid; this should be heated continuously until fused, after the addition of a little marble (to produce a continuous slight evolution of gas), in a tube of hard glass sealed at one end and connected with a further tube for conducting the gas. The silicon fluoride, which escapes in the first-mentioned operation, may also be introduced for two hours in a slow current into a test-tube containing about 0·3 grm. of aniline, dissolved in 15 c.c. of ether and 15 c.c. of alcohol. If fluorine is present, a white glittering deposit of *silicon fluoroaniline* will be formed. If this is suspended in the liquid, and three drops of a moderately concentrated solution of sodium hydroxide in absolute alcohol added, *sodium silicofluoride* will gradually subside (W. Knop [1]). The silicon fluoride reaction is not always obtained in the case of many minerals containing fluorine (Topas); it may also not occur with pure fluorides if too great an excess of the readily attacked modification of silicic acid is present. In this case, there is formed in the reaction between hydrofluoric acid and the excess of amorphous silicic acid, a non-volatile silicon oxyfluoride, the composition of which agrees approximately with the formula: $SiOF_2$ (K. Daniel [2]). Oxyfluoride is not produced, or only in quite small quantities, in the case of quartz. Daniel gives the following method of applying the test as being the most suitable. The substance is stirred in a short test-tube with 3 volumes of fine quartz powder and a little concentrated sulphuric acid, until it forms a thin paste. The tube is closed with a perforated cork with a groove in its side, through the hole of which passes a glass rod pressed out flat at one end and coated with asphalt varnish. A small drop of water is suspended from the end of the glass rod and held close to the reaction mixture, and the tube gently heated over a small flame, whereby the fluorine present is almost immediately detected by a white ring of silicic acid, $Si(OH)_4$, round the drop of water. The black coating of asphalt varnish considerably increases the sharpness of the reaction.

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[1] The statement of J. Nicklès, that every kind of sulphuric acid, in fact all acids suitable for the development of hydrogen fluoride, produce etchings on glass was not confirmed by us in the use of clock glass made of Bohemian glass, but it is wiser to ascertain, before using sulphuric acid, whether its vapours alone cannot etch the glass. Any hydrogen fluoride contained in concentrated sulphuric acid may be easily removed by diluting it with an equal volume of water, and evaporating it in a platinum dish to its former concentration.

[2] *Cf.*, however, the statements of Daniel quoted below.

8. *If silicates which are not decomposed by sulphuric acid are to be tested for fluorine, they must first of all be decomposed.* This is done by *fusing them with four parts of sodium potassium carbonate.* The mass is then treated with water, filtered, concentrated by evaporation, allowed to cool, introduced into a platinum vessel, treated with

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[1] *Chem. Zentr.*, 1882, 639.

[2] *Zeitsch. anorg. Chem.*, 38, 257 (1904).

hydrochloric acid until it is just acid, and allowed to stand until the carbon dioxide has escaped. The liquid is then treated with ammonia in excess, heated, filtered into a flask, treated while still hot with calcium chloride until silicic acid separates, and the flask then closed and allowed to stand. If, after some time, a precipitate (calcium fluoride) deposits, this should be collected on a filter and dried, freed from admixed carbonate by ignition and extraction with acetic acid, *and then tested according to the methods given in 6 and 7* (H. Rose). F. P. Treadwell recommends the following method of separating the silicic acid and precipitating fluorine as calcium fluoride. The solution of the fused mass is nearly neutralised with hydrochloric acid, treated with a large quantity of ammonium carbonate, slightly heated and allowed to stand for 12 hours. After filtration of the silicic acid, the liquid is evaporated to a small residue, and phenolphthalein solution added, whereby a red coloration is produced. Hydrochloric acid is now added with constant stirring, until the liquid is decolorised; the mixture is heated until boiling (which causes the red coloration to re-appear), again decolorised with hydrochloric acid, and this treatment continued until, on boiling, the liquid is only *pale pink*, as the carbon dioxide has been nearly all expelled. After the addition of calcium chloride, it is boiled. The resulting precipitate, which consists of calcium fluoride and calcium carbonate, is ignited on the filter, extracted with acetic acid, and then used with concentrated sulphuric acid for the etching test according to 6. The method described is suitable for use with other substances containing fluoride, *e g.* the phosphates containing calcium fluoride (apatite, etc.), after the addition of silicon dioxide, for without this addition calcium fluoride would, on fusion with alkali carbonates, be incompletely decomposed.

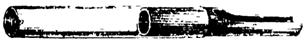

FIG. 49.

9. Small quantities of fluorides may also be readily detected in minerals, slags, etc., by means of the *blowpipe*. For this purpose, a small roll of thin platinum foil is introduced into a glass tube, as shown in Fig. 49, and in it is placed the finely ground substance, mixed with powdered alkali phosphate fused on charcoal; the blowpipe flame is then directed so that the products of combustion are conducted into the tube. In this process fluorides yield hydrofluoric acid gas, which can be recognised, not only by its penetrating odour and by the fact that the glass tube becomes dull (this is only noticeable after the tube has been cleansed and dried), but also by the yellow

coloration given to moist *Brazil wood paper*[1] when it comes into contact with the escaping acid air (Berzelius, Smithson). In the case of silicates containing fluorides, *silicon fluoride* is produced, and this also gives a yellow coloration to moistened Brazil wood paper placed in the tube, and causes silicic acid to form a deposit. After the tube has been washed and dried, it will appear opaque here and there. Minerals containing water and small quantities of fluorides, as a rule produce a yellow coloration in moistened Brazil wood paper placed in a tube, closed at one end and heated without further addition (Berzelius).

10. With regard to the methods of detecting small quantities of fluorides in rocks, which depends on the bleaching action which fluorine ion exercises on the yellow coloration given by titanic acid solution with hydrogen peroxide (G. Steiger), reference should be made to the *Zeitsch. anal. Chem.*, **55**, 398.

11. For details of the *microchemical detection* of fluorine, see Haushofer, *Mikroskopische Reaktionen*, p. 50; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 177.

SEC. 112.

Summary and Remarks on Acids, Group I.

1. The barium salts of the acids of the third division of the first group are dissolved by hydrochloric acid without the escape or separation of the acid (distinction from the acids of the fourth group); they are, therefore, re-precipitated unchanged by alkali hydroxides, as also by ammonia, when these neutralise the hydrochloric acid. The barium salts of the acids of the first division of the first group behave in a similar manner, and, if present, therefore, must be removed before a conclusion can be drawn as to the presence of phosphate, borate, oxalate, or fluorine ion from such precipitation of a barium salt. But even apart from this, no great value can be attached to this reaction for the identification of the anions mentioned, and still less for their distinction from other anions, as some of the barium salts in question, especially barium borate and barium fluoride, are not precipitated from their solutions in hydrochloric acid by ammonia, if the quantity of free acid present is at all considerable, or if an ammonium salt is present to any great extent.

2. *Boric acid* is characterised by the coloration which it imparts

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[1] Prepared by saturating fine sized paper with Brazil wood decoction.

directly as boron fluoride or as boric acid ester to an alcohol, hydrogen or non-luminous gas flame, as also by its action on turmeric paper. The latter reaction is especially suitable for the detection of very small traces. It should be noted, however, that it does not take place in the presence of nitrites and salts of other oxidising acids. If ions of heavy metals are present, either a sublimate of ammonium boron fluoride must be prepared in accordance with Sec. 109, 9, or the ions which disturb the reaction must be removed by means of hydrogen sulphide or ammonium sulphide. If a dilute solution of boric acid is to be concentrated, the free acid must be converted into borate ion by the addition of alkali hydroxide, as otherwise the greater portion of it will volatilise with the water vapour. Small quantities of boric acid may be easily and definitely detected by spectroscopic examination.

3. The detection of *phosphate ion* in compounds which dissolve in water is not difficult, and the reaction with magnesia mixture is a suitable means. The direct detection of phosphate ion in compounds which are insoluble in water is, however, not possible by means of magnesium salt solution. Ferric chloride is suitable for the detection of phosphate ion in salts of the alkaline earth metals, and especially for the separation of phosphate ion from the ions of the alkaline earth metals (Sec. 107, 9); but for the detection of phosphate ion in the presence of the ions of aluminium or iron, as also for the detection of small quantities of phosphate generally, a nitric acid solution of ammonium molybdate is especially suitable. We must, however, emphasise the fact that it is essential that the directions be strictly adhered to in the case of these two reactions. If phosphate ion is present together with the ions of the fourth, fifth, or sixth group, it can be separated from them by the method described in Sec. 107, 11 (by means of tin), or also simply by precipitating them from their solutions by means of hydrogen sulphide or ammonium sulphide.

4. *Oxalic acid* may always be readily detected by means of calcium sulphate solution in aqueous solutions of alkali oxalates. The nature of the resulting precipitate, which is insoluble in acetic acid, scarcely admits of any doubt, as a similar reaction is only given by racemic acid, an acid of rare occurrence. In cases of doubt, calcium oxalate may be easily distinguished by gentle ignition in the absence of air from calcium racemate, which is decomposed with the separation of a considerable quantity of carbon; calcium racemate may also be dissolved in cold sodium or potassium hydroxide solution, but this is not the case with calcium oxalate. Further,

the behaviour of oxalates towards sulphuric acid or manganese dioxide and sulphuric acid is a sufficiently confirmatory test. The oxalate ion is detected with the greatest certainty in insoluble salts, when they are decomposed by boiling them with a solution of sodium carbonate or by means of hydrogen sulphide or ammonium sulphide (Sec. 110, 14) Finally, it must be mentioned that there are soluble oxalates which are not precipitated by calcium salts, namely, chromic oxalate and ferric oxalate. This fact depends on the formation of complex anions, the calcium salts of which are soluble. Oxalate ion may be detected in them according to Sec. 110, 9 or 10.

5. *Fluorine ion* may be easily detected in salts decomposable by sulphuric acid, but it must be remembered that too large a quantity of sulphuric acid has a preventive influence on the ready evolution of hydrogen fluoride, and thus impairs the sensitiveness of the reaction, so that no clear etching of the glass will take place if, instead of hydrogen fluoride, only silicon fluoride is formed, consequently, for the sake of certainty in the case of compounds rich in silicic acid, one of the reactions mentioned in 7 should be used as well as those described in Sec 111, 6. Fluorine is often overlooked in silicates which are not decomposed by sulphuric acid owing to the omission of a careful examination according to the methods mentioned in Sec. 111, 8.

SEC. 113.

Phosphorous acid, H_2PHO_3 (Phosphite ion, PO_3H'').

1. The *anhydride of phosphorous acid*, P_4O_6 (phosphorus trioxide), is a white, sublimable powder, which burns when heated in the air. With a little water, it forms phosphorous acid, a viscous liquid, which, on standing for some time, crystallises and decomposes, when heated, into phosphoric acid and gaseous hydrogen phosphide, which does not ignite spontaneously. Phosphorus trioxide is readily soluble in water, and is poisonous. Phosphorous acid is dibasic, behaves in aqueous solution in the same way as a moderately strong acid, and, on dissociation, is only reduced one stage.

2 Of the *salts* (phosphites), those of the alkali metals dissolve readily in water, all the others with difficulty; the latter dissolve in dilute acids. All these salts decompose on ignition, leaving a residue of pyrophosphates, while hydrogen or a mixture of hydrogen and hydrogen phosphide escapes.

3. *Silver nitrate* produces, especially on the addition of ammonia and when heated, a precipitate of *metallic silver.*

4. *Mercurous nitrate* produces under similar conditions a precipitate of metallic *mercury.*

5. Phosphite ion precipitates after some time, more rapidly when

heated, *mercurous chloride* from a solution containing an excess of *mercuric chloride*.

6. *Barium chloride* and *calcium chloride* produce, on the addition of ammonia in not too dilute solutions, white precipitates, soluble in acetic acid.

7. *Magnesia mixture* gives a precipitate only in somewhat concentrated solutions.

8. *Lead acetate* precipitates *white lead phosphite*, insoluble in acetic acid.

9. A *solution of ammonium molybdate* in nitric acid produces, on heating, a yellow crystalline precipitate, the composition of which agrees with the formula $(NH_4)_2[HP(Mo_2O_7)_3].2H_2O$. Rosenheim, Weinberg and Pinsker, *Zeitsch. anorg. Chem.*, **84**, 217; *Chem. Zentr.*, 1914, I., 1064.

10. On boiling a solution of a phosphite with excess of *sulphur dioxide*, phosphate ion is formed and sulphur separates.

11. When brought into contact with *zinc* and dilute *sulphuric* acid, phosphite ion produces hydrogen containing *hydrogen phosphide*, which therefore fumes in the air, burns with an emerald green flame, and precipitates silver and silver phosphide from a solution of silver nitrate. Nitric acid influences the formation of hydrogen phosphide. If it is present in small quantity only, a little ferrous chloride should be added first, and the zinc after a little while. Instead of causing the gas containing hydrogen phosphide to act upon silver nitrate solution, it may be brought into contact with filter paper saturated with such solution, or sized paper moistened with it (H. Hager). If the quantity of phosphite ion is small the silver paper will only become black after some hours. It should be noted that this blackening of the paper may also be caused by hydrogen sulphide or hydrogen arsenide.

Fourth Division.

Of the first group of inorganic acids.

Sec. 114.

(a) **Carbonic acid,** H_2CO_3 (Carbonate ion, CO''_3, hydrogen carbonate ion, HCO'_3).

1. Carbon is a solid, tasteless, and odourless substance. It only melts and volatilises at the very highest temperatures (Despretz). All carbon is combustible, and when burnt with a constant supply of oxygen or air, forms carbon dioxide. In the form of the *diamond*, carbon is crystalline, transparent, colourless, exceedingly hard and difficult to burn; in the form of *graphite* it is opaque, greyish-black in colour, soft, difficult to burn, and greasy to the touch; in the form of *charcoal*, obtained by the decomposition of organic substances, it is black, opaque, non-crystalline, sometimes compact, lustrous, and difficult to burn, sometimes, however, dull, porous, and easily burnt.

2. *Carbonic acid*, H_2CO_3, is not known in a pure condition; it exists only in aqueous solution and decomposes (completely when boiled) into water and anhydride. At the ordinary temperature and the ordinary air pressure, *carbonic anhydride* (*carbon dioxide*, according to the old nomenclature, carbonic acid), CO_2, is a colourless gas, which is much heavier than air, so that it may be poured out of one vessel into another. Carbon dioxide has a faint odour and an acid taste; it turns moistened litmus paper red, but the red coloration disappears on drying; it does not support combustion, but immediately extinguishes a burning taper. Carbon dioxide is readily absorbed by alkali hydroxide solution; it dissolves to a considerable extent in water *Carbonic acid water* has an acid, "prickly" taste, turns litmus paper red temporarily, imparts a wine-red colour to litmus tincture, and loses its carbon dioxide when shaken in a flask half filled with air, and more completely when heated Carbonic acid belongs to the very weak acids, being about 60 times as weak as acetic acid, and only dissociated to about 0·25 per cent. in 0·1 *N*-solution. The dissociation constants are: For the first stage apparently[1] $K_1 = 3.01 . 10^{-7}$, for the second $K_2 = 6 . 10^{-11}$.

3. *Carbonic acid* forms, as a dibasic acid, normal and acid salts (carbonates and hydrogen carbonates). The carbonates of the alkali metals melt on heating, and are slightly decomposed at a high temperature; the carbonates of the alkaline earth and heavy metals decompose, on ignition, into carbon dioxide and the oxides of the metals All the carbonates of metals the oxides of which are not coloured are white or colourless. Of the carbonates, only those of the alkali metals are soluble in water, and owing to hydrolysis their solutions give very strongly alkaline reactions. Of the hydrogen carbonates, those of the alkaline earth metals and of several heavy metals, as well as those of the alkali metals, dissolve in water; their solutions are decomposed on boiling, with the formation or separation of normal carbonates.

4 *The carbonates are decomposed by* **all free acids** *which are* soluble in water, with the exception of hydrocyanic acid; as a rule, this takes place in the cold, but in the case of many of the natural carbonates, *e.g* magnesite, only on heating. *In this process carbon dioxide escapes with effervescence* as a colourless, practically odourless, gas, which temporarily reddens litmus. In this decomposition, especially in the case of alkali carbonates, an excess of the acid should be used, as the addition of too small a quantity of acid will often

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[1] *Cf.* A. Thiel and R. Strohecker, *Zeitsch. anal. Chem.*, **53**, 647.

not produce effervescence, owing to the formation of hydrogen carbonates. Substances which are to be tested by this method for carbonate ion should first be heated with a little water, so that no mistake may be made owing to escaping air bubbles. If there is the risk of carbon dioxide escaping when boiled with water, lime-water should be used instead of pure water. To confirm the fact that the escaping gas is carbon dioxide by a direct test, it should be introduced into lime or baryta water, or a glass rod dipped into baryta water and inserted into the test-tube in such a way that its lower end reaches nearly to the liquid. If the gas is carbon dioxide, the lime or baryta water will become turbid (see 5).[1] It should be noted that lime and baryta water are rendered somewhat turbid even by the carbon dioxide contained in the air

5. When **lime water** and **baryta water** come in contact with carbon dioxide or soluble carbonates, they yield *white precipitates of calcium carbonate*, $CaCO_3$, or *barium carbonate*, $BaCO_3$. In testing lime water or baryta water for free carbon dioxide, an excess of the reagents should always be used, as the hydrogen carbonates of the alkaline earth metals are soluble in water. After separation from the liquid, the precipitates which are formed dissolve in acids with effervescence; no precipitate is formed by ammonia in the solution after the carbon dioxide has been completely expelled by boiling. For the detection of the minutest traces of carbonate ion, the apparatus shown in Fig. 50 may be recommended, a detailed description of which is hardly necessary.

The tube *a* contains soda-lime; a fairly large quantity of the substance to be tested for carbonate ion is introduced with a little water into *b*, *c* remaining empty for the time being. The apparatus is filled by suction with air, free from carbon dioxide, by means of a water pump or an aspirator at *d*, a little lime or baryta water filtered into *c*, and a small quantity of hydrochloric acid poured into the funnel, whilst a slow stream of the air (freed from carbon dioxide) is allowed to pass through the apparatus and *b* gently heated. As lime-water dissolves very small quantities of calcium carbonate, it is advisable to saturate it by digesting it with that salt for some time (Welter, Berthollet).

6. **Calcium** and **barium chloride** *produce, immediately with alkali*

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[1] The sensitiveness of the reaction may be increased by the use of the apparatus mentioned by O. Rossler (*Ber.*, 20, 2630), but we prefer to use the apparatus described in 5 in cases in which it is a question of the detection of very small quantities of carbon dioxide.

carbonates, only on heating with hydrogen carbonates (*if dilute*), *precipitates of calcium or barium carbonate*, $CaCO_3$, or $BaCO_3$. No precipitation takes place with free carbonic acid (a solution of carbon dioxide in water).

7. *An aqueous solution of lead chloride produces in aqueous solutions* of alkali carbonates and hydrogen carbonates of the alkali and alkaline earth metals, even when very dilute, a *milky white precipitate of lead carbonate*, $PbCO_3$ (H. Schulze). Free carbonic acid influences or prevents the reaction. Acetic acid dissolves the precipitate. (Distinction from lead sulphate.)

8. For the detection of *free carbonic acid in the presence of hydrogen carbonates*, a solution of 1 part of *rosolic acid* in 500 parts of 80 per cent. alcohol (which has been treated with baryta water until a reddish coloration begins to appear) may be used. On adding—for instance, in testing spring water—about 0·5 c.c. of *rosolic acid solution* to 50 c.c. of water, a colourless, or at the most pale yellow liquid is obtained if the water contains free carbonic acid and no large quantities of hydrogen carbonate ion; [1] if, however, it contains no free carbonic acid, but only hydrogen carbonates, the liquid becomes red (M. v. Pettenkofer). *Phenolphthalein* behaves in the same manner as rosolic acid. A liquid to which phenolphthalein has been added, and which contains hydrogen carbonate, but *no free carbonic acid*, is *red*. *Free carbon dioxide causes the colour to disappear.*

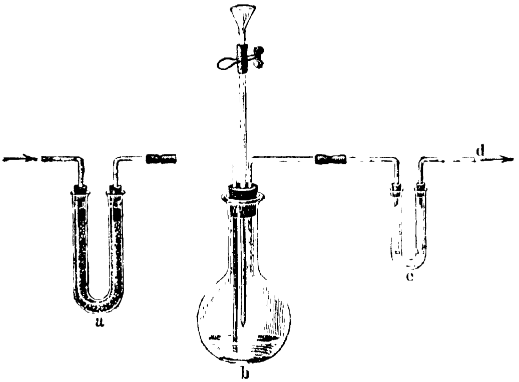

FIG. 50.

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[1] J. Tillmans and O. Heublein, *Zeitsch. anal. Chem.*, **51**, 691.

9. The detection of *free carbonic acid* or of *hydrogen carbonates in the presence of carbonates* is based on the fact that *Nessler's ammonia reaction* (see Sec. 30, 10) does not take place when free carbonic acid or hydrogen carbonates are present (*cf.* Salzer, *Zeitsch. anal. Chem.*, **20**, 227).

10. For details of the *microchemical detection* of carbonic acid, see Haushofer, *Mikroskopische Reaktionen*, p. 66; Behrens-Kley, *Mikroskopische Analyse*, 3rd ed., p. 167.

Appendix.

The reactions of the carbonates are also produced by **percarbonates** (percarbonate ion, $C_2O''_6$), as percarbonates in solution are decomposed into carbonate and hydrogen peroxide

The oxidising action of percarbonates is characteristic of them.

When treated with *potassium dichromate* and shaken with ether, percarbonates give a blue coloration to the layer of ether. They do not liberate iodine from *potassium iodide* in neutral solution, but do so on acidification.

Potassium permanganate solution is decolorised, with the separation of manganese dioxide; the separation does not take place in acid solution.

Percarbonates give no reaction with *benzidine solution.* With *titanium trichloride,* $TiCl_3$, they produce a red coloration (Monnier, *Chem. Zentr.*, 1917, I., 691).

With manganous, nickelous, and cobaltous salts, dark precipitates of higher oxides are produced. *Cerous chloride* is coloured yellow (*cf.* also Lenz and Richter, *Zeitsch. anal. Chem.*, **50**, 537).

SEC. 115.

(b) Silicic acid, (orthosilicic acid, H_4SiO_4, and metasilicic acid, H_2SiO_3; orthosilicate ion, SiO''''_4, metasilicate ion, SiO''_3).

1. Silicon is known in an amorphous and a crystalline modification; in the amorphous condition it is a brown powder, which is oxidised on ignition in the air. Crystalline silicon forms black, metallic, lustrous octahedra, and remains unchanged on ignition in the air. Silicon is not attacked by acids or even by concentrated aqueous hydrofluoric acid; on the other hand, it is dissolved by a mixture of nitric acid and hydrofluoric acid; it is readily dissolved by hot solutions of potassium or sodium hydroxide, with the liberation of hydrogen and the formation of alkali silicates; it can be volatilised

in a current of chlorine as silicon chloride. Silicon combines with many metals to form *silicides*, which can be decomposed by acids. *Silicon carbide* (carborundum), SiC, is stable on ignition, and is very resistant to acids ; it is decomposed on fusion with sodium hydroxide or sodium carbonate.

3. *Orthosilicic acid*, H_4SiO_4, and *metasilicic acid*, H_2SiO_3, are produced in the form of a gelatinous mass by the hydrolysis of silicon fluoride, and by the decomposition of alkali silicates with dilute acids ; they are both easily soluble in water and acids, with the formation of colloidal solutions ; on drying they lose water, and on ignition are converted into *silicic anhydride*, *silicon dioxide* $(SiO_2)_n$. Silicon dioxide, often called *silicic acid* according to the older nomenclature, is colourless or white, does not change even in the hottest part of a Bunsen or blowpipe flame, and is infusible. It melts in an oxyhydrogen flame. It volatilises at a very high temperature (E. Cramer, H. Moissan). It occurs in the crystallised (rock crystals), crystalline (quartz), and amorphous forms. It is insoluble in water and acids (with the exception of hydrofluoric acid, which dissolves amorphous silicon dioxide easily, and the crystalline form with more difficulty), whereas ortho- and metasilicic acids are soluble in them, although only at the moment of separation. Amorphous silicon dioxide and the silicic acids dissolve in hot aqueous solutions of alkali hydroxides and alkali carbonates ; this is not the case with the crystalline silicon dioxide, or only when it is very finely divided (G. Lunge and C. Millberg). Ammonia solution dissolves gelatinous silicic acid fairly easily, dry silicic acid and amorphous silicon dioxide more sparingly, and crystallised silicon dioxide very slightly. Silicic acid belongs to the weakest inorganic acids. The *salts* of silicic acid (silicates) are derived from ortho- and metasilicic acid, as also from various polysilicic acids. Of the silicates, only those of the alkali metals are soluble in water ; they are obtained by the fusion of silicon dioxide or silicic acid with alkali hydroxides or alkali carbonates, and owing to hydrolysis give a strongly alkaline reaction.

3. *The solutions of alkali silicates are decomposed* **by all acids**. If a **large quantity of hydrochloric acid** is added, *all at once*, even to concentrated solutions, *the separated silicic acid remains in solution* ; if, on the other hand, *the hydrochloric acid is added drop by drop while the solution is being stirred, the greater portion of the silicic acid will separate in a gelatinous form*. The more dilute the liquid, the more the silicic acid remains in the colloidal condition ; no precipitation takes place in very dilute solutions *If, however, the solution of an*

alkali silicate, treated with an excess of hydrochloric or nitric acid, is evaporated to dryness, silicic acid will separate in the proportion in which the acid escapes ; when the residue is dried at 100° *and then treated with hydrochloric acid and water,*[1] *the silicic acid is left in the form of an insoluble white powder of silicon dioxide* (*see* 4). If the solutions of alkali silicates are treated with *ammonium chloride*, silicic acid gel containing alkali will be precipitated (if the solutions are not too dilute) ; heating promotes the separation. Silicic acid is less completely separated by *ammonium carbonate ;* the last traces of silicic acid may be removed by boiling the mixture with an *ammoniacal zincate solution*, whereby zinc silicate and zinc hydroxide are precipitated.

4. *Some of the silicates insoluble in water are decomposed by hydrochloric or nitric acid ; others are not attacked by these acids* (*or scarcely so*) *even when boiled.* During decomposition of the former, the greater portion of the silicic acid generally separates as gel, less frequently as pulverulent silicic acid. *To separate it entirely*, the hydrochloric acid solution, together with the precipitate of silicic acid suspended in it, is *evaporated to dryness, heated*, while being stirred, *at an even temperature* (*slightly exceeding the boiling point of water*) until no more acid vapours escape, *the residue moistened with hydrochloric acid, heated with water, and the undissolved silicon dioxide filtered off* from the acid liquid containing the metal ions Of the silicates not decomposable by hydrochloric acid, many, *e.g.* kaolin, are completely decomposed when heated with a mixture of 8 parts of concentrated *sulphuric acid* and 3 parts of water, whilst pulverulent silicon dioxide is separated ; many others are, to a certain extent, attacked by this mixture. If silicates, which are not decomposed when boiled with hydrochloric or sulphuric acid in an open vessel at the ordinary atmospheric pressure, are heated in finely powdered form with acids in strong glass tubes (closed by fusion) in an air or paraffin oil bath at 200° to 210°, most of them are completely decomposed.

5. On fusing a finely ground silicate with 4 parts of **alkali carbonate** (preferably potassium sodium carbonate) until carbon dioxide no longer escapes, and *boiling the mass with water, the greater portion of the silicate ion will dissolve as alkali silicate*, whilst the carbonates of the alkaline earth metals, the earths (with the exception of aluminium and beryllium oxide, which are more or less completely dissolved as aluminate and beryllate ions), and the oxides of the heavy metals remain undissolved. *On treating the fused*

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[1] *Cf.* p. 36, second paragraph.

mass with water and (without filtration) adding hydrochloric or nitric acid until the reaction is strongly acid, and treating the liquid as in 4, *silicon dioxide remains undissolved, while the metal salts dissolve.* If the mass is fused with 4 parts of *barium hydroxide*, digested with water, hydrochloric or nitric acid added, and the acid solution treated according to 4, silicon dioxide is also separated The metal ions, especially those of the alkali metals, will then be found in the filtrate.

If a silicate is ground up with 1 part of *ammonium chloride* and 8 parts of calcium carbonate, and the mixture heated in a platinum crucible, gently at first, and then with a full flame, the silicate is decomposed The solution obtained on treating the residue, left on ignition, with hot water contains alkali metal ions as well as the dissolved calcium ions (J L Smith).

6 *By treating silicon hydroxide with* **hydrofluoric acid** *in concentrated aqueous solution or as a gas, silicon fluoride escapes :*

$$SiO_2+4HF=SiF_4+2H_2O$$

dilute acid dissolves it in the form of silicohydrofluoric acid :

$$SiO_2+6HF=H_2SiF_6+2H_2O$$

On evaporating the solution to dryness, there will be no residue if the silicon dioxide and the hydrofluoric acid were pure and the latter predominated. When silicates are treated with hydrofluoric acid, silicofluorides are formed, $CaSiO_3+6HF=CaSiF_6+3H_2O$, which are converted into sulphates when evaporated with concentrated sulphuric acid, whilst hydrogen fluoride and silicon fluoride escape. The resulting sulphates may be used as a suitable material for the detection of alkali metal ions. Further, when a silicate is mixed with 3 parts of *ammonium fluoride* or with 5 parts of *fluorspar powder*, stirred to a paste with *concentrated sulphuric acid*, and heated until vapours no longer escape, the silicic acid will all volatilise as silicon fluoride. The residue will contain the cations in the form of sulphates, in admixture with calcium sulphate, when fluorspar was used.

All the tests described in 6 must be carried out in platinum vessels, and all evaporations must take place in a fume cupboard or preferably in the open.

7. When one part of finely powdered silicon dioxide or silicate is mixed with about 2 parts of powdered sodium aluminium fluoride free from silicic acid, Na_3AlF_6, *cryolite*, or with *fluorspar*, CaF_2, *the mixture gently heated* (so that it does not spirt) with 4 to 6 parts of *concentrated sulphuric acid* in a platinum crucible, and a strong

platinum wire with a *drop of water* suspended from its round, freshly-ignited loop is held close to the surface, the drop of water will soon be covered with a white coating of silicic acid, owing to the decomposition of the escaping silicon fluoride (Barfoed). *Cf.* Sec. 111, 7.

The detection of silicon dioxide by its conversion into silicon fluoride is not particularly sensitive in the examination of quartz, as hydrofluoric acid has a very slow action on quartz powder. K Daniel [1] recommends, therefore, that every substance to be tested for silicic acid should be fused with 3 times its quantity of sodium potassium carbonate. The fused mass is taken up with a little hot water and almost completely evaporated with dilute sulphuric acid in a platinum crucible. When cold, the residue is treated with 3 times its quantity of calcium fluoride, a little magnesite, and sufficient concentrated sulphuric acid to form a thin paste, the whole stirred with a platinum wire, and a small drop of water placed on the inside of the lid, which should be partly coated with asphalt lacquer. After replacing the lid, the crucible is heated on an asbestos plate over a small flame, and the lid lifted from time to time, in order that the occurrence of the reaction may not be missed. The reaction becomes noticeable by the appearance of a white edge of silicic acid round the drop of water; in the presence of considerable quantity of silicic acid the whole drop becomes gelatinous.

8. *On fusing silicon dioxide or a silicate* of the alkaline earth metals or heavy metals with **sodium carbonate** on a loop of platinum wire, *frothing* takes place in the melting bead, owing to the escape of carbon dioxide. The bead obtained with pure silicon dioxide is always clear while hot, that produced by silicates only clear when they contain a large quantity of silicate ion (as *e.g.* the felspar minerals). The question as to whether the bead remains clear or not on cooling depends on the proportional relationship between the silicate ion, and sodium ion, or other metal ions.

9. **Melting alkali phosphate** only dissolves silicon dioxide in small quantities. If, therefore, a *silicate* (but not precipitated amorphous silicic acid), preferably in small pieces or splinters, is fused with alkali phosphate on platinum wire, although the cations dissolve, *the greater portion of the silicon dioxide remains, as a rule, undissolved*, and floats in the clear bead as a more or less transparent mass in the form of the piece of silicate used, forming the so-called "*silicic skeleton.*"

The reaction is not very trustworthy, as many silicates, *e.g.* zeolites, dissolve, forming a clear solution in the bead, whereas various minerals free from silicon show a similar behaviour to that of the characteristic "skeleton formation" (K. Haushofer, J. Hirschwald, *Zeitsch. anal. Chem.*, **29**, 318).

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[1] *Zeitsch. anorg. Chem.*, **38**, 302 (1904); *cf.* also J. Petersen, *Zeitsch. anal. Chem.*, **43**, 619 (1904).

10. With regard to the *microchemical detection* of silicic acid, see Haushofer, *Mikroskopische Reaktionen*, p. 120; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 106; N. Schoorl, *Zeitsch. anal. Chem.*, **48**, 672.

SEC. 116.

Summary and Remarks on Acids, Group I.

1. *Free carbon dioxide* may be easily recognised by its behaviour towards lime or baryta water, and the *carbonates* by the fact that when treated with acids they evolve an almost odourless gas. Many natural carbonates, *e.g.* magnesite, are only decomposed by acids when heated. If compounds are being dealt with from which other gases are simultaneously developed, the gas should be tested with lime or baryta water.

2. *Silicic acid* may generally be recognised by its behaviour, and that of its salts towards alkali phosphate (*cf.*, however, the end of Sec. 115, 9). Moreover, it is distinguished, in the form in which it is obtained in analysis, from all other substances, by the fact that it is insoluble in acids (with the exception of hydrofluoric acid) or in fused potassium hydrogen sulphate, but dissolves completely in boiling solutions of alkali hydroxides and alkali carbonates; it is also distinguished from many others (especially alumina and titanium dioxide) in that it evaporates completely when evaporated in a platinum dish with hydrofluoric acid, after the addition of sulphuric acid (or with ammonium fluoride and sulphuric acid).

SECOND GROUP OF INORGANIC ACIDS.

Anions which are precipitated by silver nitrate, but not by barium chloride.

Hydrochloric acid, hydrobromic acid, hydriodic acid, hydrocyanic acid, ferro- and ferrihydrocyanic acids, thiocyanic acids, hydrosulphuric acid, or chlorine ion, bromine ion, iodine ion, cyanogen ion, ferrocyanogen ion, ferricyanogen ion, thiocyanogen ion, sulphide ion (nitrous acid, hypochlorous acid, hypophosphorous acid, hydronitric acid, or nitrite, hypochlorite, hypophosphite, azide ions).

The silver compounds corresponding to the acids mentioned are all insoluble in dilute nitric acid.

SEC. 117.

(a) Hydrochloric acid, HCl (Chlorine ion, Cl').

1. *Chlorine* is a heavy, yellowish-green gas, of an unpleasant suffocating odour, and with an extremely injurious action on the respiratory organs; it bleaches vegetable colouring matters (litmus, indigo blue, etc.), is non-combustible, and supports the combustion of only a few substances. Finely divided antimony, tin, etc., ignite in it and burn to chlorides. It dissolves in water in considerable quantity. The *chlorine water* thus formed is pale yellowish-green, smells strongly of the gas, bleaches vegetable colouring matters, and decomposes slowly under the action of light, with the formation of the ions of hydrochloric acid and hypochlorous acid, HClO, the latter then decomposing again into hydrogen chloride and free oxygen. Chlorine water loses its odour when shaken with mercury, in which process the latter is partly converted into mercurous chloride; any hydrochloric acid contained in chlorine water may be recognised by its acid reaction. Small quantities of *free chlorine* may be easily detected in a liquid, if the latter is added to dilute, slightly bluish *indigo solution*, which loses its colour by the action of the free chlorine; or (in the absence of nitrous acid and other compounds which decompose iodides) if it is added to a dilute solution of *potassium or zinc iodide*, mixed with *starch paste*, whereby a *blue coloration* appears (see Sec 119, 11); the latter reaction may also be carried out with *potassium iodide starch paper*. Small quantities of free chlorine in an *acetic acid solution of aniline and o-toluidine* produce a *blue coloration*, which turns red on standing. The reaction also appears when a strip of paper moistened with the reagent is exposed to chlorine vapour. (Free bromine produces a white precipitate with the reagent.) To prepare the reagent, 100 c.c. of a saturated aqueous solution of aniline are mixed with 20 c.c. of a saturated aqueous solution of *o*-toluidine and 30 c.c. of glacial acetic acid (A. Villiers and M. Fayolle, *Zeitsch. anal. Chem.*, 34, 607).[1] If a strip of paper moistened with a solution of *potassium bromide* is dried, then dipped into an 0·01 per cent. of an ammoniacal alcoholic *solution of fluorescein*, and, when dry, exposed to the vapour of free chlorine, the paper assumes a *pink* coloration, because the bromine liberated from the bromide converts fluorescein into eosin (*cf.*

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[1] Ferric chloride and nitrites also produce a blue coloration (Ellms and Hauser, *Chem. Zentr.*, 1914, II., 506).

Sec. 118, 8. D. Ganassini, *Chem. Zentr.*, 1904, I., 1172). On adding a solution containing free chlorine to a sulphuric acid *solution of magenta*, treated with acetic acid, the mixture becomes *yellow*; when the liquid is shaken with chloroform, this absorbs the coloured products. (In the presence of bromine a reddish-violet coloration is produced.) To prepare the reagent, 10 c.c. of a 0·1 per cent. solution of magenta is added to 100 c.c. of 5 per cent. sulphur dioxide solution, and 25 c.c. of the decolorised solution mixed with 25 c.c. of glacial acetic acid and 1 c.c. of sulphuric acid (G. Denigès and L. Chelle, *Chem. Zentr.*, 1913, I., 127). Free chlorine is converted, when treated with an excess of *ammonia*, with alkaline *hydrogen peroxide solution*, with *sulphur dioxide*, or with *zinc* and *sulphuric acid*, into chloride or hydrochloric acid, and then shows the reaction of chlorine ion described below.

2. *Hydrogen chloride* (hydrochloric acid), HCl, is, at the ordinary temperature and atmospheric pressure, a colourless, suffocating and irritating gas, which is readily soluble in water and forms dense fumes in moist air (especially with ammonia vapour). The concentrated aqueous solution (fuming *hydrochloric acid*) loses a large portion of its gas when heated. Aqueous hydrochloric acid is the typical strong acid. It is dissociated to the extent of about 92 per cent. in 0·1 *N*-solution, even at 18°.

3. The *salts* of hydrochloric acid (*chlorides*) are easily soluble in water, with the exception of lead, silver, cuprous, mercurous, and thallous chlorides, as also bismuthyl chloride and antimonyl chloride. All chlorides which dissolve with difficulty are, with the exception of silver chloride, dissolved by *aqua regia*. Most chlorides are white or colourless, many volatilise on heating without decomposition, others are decomposed on ignition, and many resist the action of a moderate ignition temperature. The dry soluble chlorides are decomposed by concentrated sulphuric acid with the evolution of hydrogen chloride gas, since sulphuric acid, although somewhat the weaker acid, is much less volatile than hydrochloric acid. In the same way, dissolved chlorides are converted into sulphates on evaporation with sulphuric acid, whilst hydrochloric acid escapes.

4. *Hydrochloric acid and nearly all solutions of chlorides yield with* **silver nitrate,** *even when very dilute, a white precipitate of silver chloride*, AgCl (*cf.* Sec. 70, 8), which becomes first violet and then black in the light, is *insoluble in dilute nitric acid*, but *readily soluble in ammonia solution*, and in potassium cyanide and potassium thiosulphate solutions; this precipitate dissolves also in a boiling

solution of ammonium sesquicarbonate[1] (H. Hager), and melts on heating, without decomposition. Chlorine ion is incompletely precipitated by silver nitrate from a solution of green chromic chloride (Peligot) and of mercuric chloride; it is not precipitated from a solution of molybdenyl chloride, MoO_2Cl_2, in sulphuric acid (Blomstrand). In the case of strong reducing compounds such as ferrous sulphate, the test for chlorine must be carried out with silver nitrate in strong nitric acid solution, as otherwise a separation of metallic silver will occur; it is best to precipitate it from such a solution with sodium carbonate, to filter the liquid, to test the filtrate with silver nitrate after acidification with nitric acid. Silver nitrate precipitates from auric chloride solution, even in the presence of nitric acid, an ochre-yellow double compound, containing silver, gold, and chlorine. Platino-hydrochloric acid behaves in a similar manner.

5. **Mercurous nitrate** and **lead acetate** produce in solutions containing free hydrochloric acid or chlorides precipitates of *mercurous chloride*, Hg_2Cl_2, and *lead chloride*, $PbCl_2$. For the properties of these precipitates, see Secs. 71, 6, and 72, 9. Lead acetate precipitates auric lead chloride from auric chloride solution.

6. When a mixture of one volume of 10 per cent *cupric sulphate* solution and 10 volumes of *concentrated sulphuric acid* is treated with a few drops of a chloride solution, a yellow precipitate is formed (bromides give a black precipitate (G. Viard). See Sec. 75, 13).

7. Elementary *chlorine* is liberated from hydrochloric acid and chlorides by oxidising reagents, such as *potassium dichromate*, *potassium permanganate*, and the *peroxides of heavy metals* (*cf.* Oxidation, Sec. 16). *Thus, on heating hydrochloric acid with* **manganese dioxide** (black oxide of manganese) or **lead peroxide,** or on heating *chlorides* with **manganese dioxide** or **lead peroxide,** and fairly concentrated **sulphuric acid,** *chlorine gas* is evolved, which can be easily recognised by its yellowish-green colour, its odour, and its bleaching action on vegetable colouring matters. To identify the gas, a strip of moist litmus paper, or moist paper coloured with indigo solution, should be exposed to its action. On heating chlorides with *manganese dioxide* or *lead peroxide and acetic acid, no* chlorine is liberated. (Distinction from bromine and iodine.) In the oxidation of hydrochloric acid by nitric acid, there is formed, in addition to free chlorine, nitrosyl chloride, $3HCl+HNO_3=Cl_2+NOCl+2H_2O$, owing to

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[1] To prepare this, one part of commercial transparent ammonium carbonate is dissolved in 9 parts of water at the ordinary temperature, and to each 10 c.c. of the liquid 5 drops of aqueous ammonia solution of sp. gr. 0·96 are added.

by-reactions. A mixture of one volume of concentrated nitric acid and three volumes of concentrated hydrochloric acid is termed *aqua regia*, owing to its power to dissolve gold and platinum. Its strong oxidising action is due to the fact that chlorine is present in its nascent condition (see Sec. 16, p 63).

8. When a solid chloride is ground with half its weight or a little more of potassium dichromate, *the whole dry mixture*[1] *covered* in a small dry retort provided with a tubulure *with concentrated sulphuric acid and gently heated, chromyl chloride*, CrO_2Cl_2, is formed as a deep *brownish-red gas*. It condenses to a liquid of the same colour, and distils into the receiver. *If this distillate is mixed with an excess of ammonia*, a liquid, coloured yellow by the ammonium chromate, is obtained in accordance with the equation:

$$CrO_2Cl_2+4NH_4OH=2NH_4Cl+(NH_4)_2CrO_4+2H_2O$$

This yellow colour turns reddish-yellow on the addition of acid, owing to the formation of dichromate ion. As a further confirmation, the solution may be poured into hydrogen peroxide solution with a layer of ether over it, and shaken, when the chromate ion will be recognised by the blue coloration of the layer of ether. *The detection of chromate ion indicates the presence of chlorine ion*, as no volatile chromium compound can be formed without chloride. In testing iodides for chlorides, the use of alkali hydroxide solution is preferable for the decomposition of the chromyl chloride, as iodine forms explosive compounds with ammonia. Sparingly soluble chlorides, such as silver and mercurous chloride, and also mercuric chloride, do not form chromyl chloride; its formation is influenced by the presence of nitrites, nitrates, and chlorates.

9. Chlorine ion is detected in *chlorides* which are *insoluble* in water and nitric acid, by boiling them with *sodium carbonate solution* or *fusing* them with an *alkali carbonate* (preferably sodium carbonate). Water will then extract the resulting alkali chloride, together with the excess of alkali carbonate from the fused mass. *Silver chloride* is only decomposed by *fusion*, or by treatment with *zinc* and dilute *sulphuric acid*.

10. Many non-electrolytes, such as the acid chlorides (PCl_3, $AsCl_3$, etc.), which do not show the reactions of chlorine ion, are decomposed by water with the formation of hydrochloric acid, and may then be detected as such. Organic chloro-substitution products

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[1] The reaction is only successful in the absence of moisture, as otherwise the chromyl chloride would be decomposed.

should be treated according to the methods of organic analysis, that is to say, either fused with alkali carbonate or ignited with lime, or else heated with nitric acid and silver nitrate in a glass tube closed by fusion, at a high temperature, whereby silver chloride is formed.

11. On dissolving sufficient *cupric oxide* on a platinum wire in the oxidation area of the gas flame in a bead of **alkali phosphate,** so that it becomes nearly opaque, then bringing a trace of a substance containing chlorides into contact with the still fused bead, and heating it in the *reduction area* of the flame, the bead will be surrounded with a *fine blue flame,* shading into purple, so long as chloride is present (Berzelius).

12. With regard to the *microchemical detection* of chlorine ion, see Haushofer, *Mikroskopische Reaktionen*, p. 47; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 172; A. Percy Smith, *Pharm. Zentralh.*, **27**, 638.

SEC. 118.

(b) **Hydrobromic acid,** HBr (Bromine ion, Br').

1. *Bromine* is a heavy, dark brownish-red liquid. It has a very unpleasant odour, similar to that of chlorine, boils at 63°, and evaporates rapidly, even at the ordinary temperature. *Bromine vapour* is brownish-red and very poisonous. Bromine, like chlorine, bleaches vegetable colouring matters; it dissolves fairly easily in water, more readily in concentrated hydrochloric acid and in alcohol, and very easily in ether, carbon bisulphide, and chloroform to form yellowish-red solutions. Ether, carbon bisulphide, and chloroform, when shaken with an aqueous solution of bromine, extract the bromine from it. Bromine water, like chlorine water, is decomposed by the action of light; when shaken with mercury, the free bromine is absorbed, and any hydrobromic acid present may then be detected by the acid reaction. Free bromine is converted into hydrobromic acid in the same way as free chlorine into hydrochloric acid (*cf.* Sec. 117, at the end of 1).

2. *Gaseous hydrogen bromide,* HBr, *aqueous hydrobromic acid,* and the *bromides* closely resemble in their general behaviour the corresponding chlorine compounds. Hydrobromic acid is a strong acid, and, at all events in aqueous solution, is as strongly dissociated as hydrochloric acid; it is more easily oxidised than the latter, and even on standing in the air it slowly turns yellow. Dry bromides, or their concentrated solutions, when treated with concentrated

sulphuric acid, evolve hydrogen bromide, which partially reacts with sulphuric acid to form sulphur dioxide and *free bromine*.

3. **Silver nitrate** produces in aqueous solutions of hydrobromic acid or bromides a *yellowish-white precipitate of silver bromide*, AgBr, which turns grey in the light, is *insoluble in dilute nitric acid*, and scarcely soluble in a boiling solution of ammonium sesquicarbonate (H. Hager); see p. 116, footnote. *Aqueous ammonia solution dissolves silver bromide, but with greater difficulty than silver chloride.* Silver bromide dissolves readily in potassium cyanide and sodium thiosulphate solutions.

4. *Palladous nitrate, but not palladous chloride*, produces in neutral solutions of bromides (immediately if they are concentrated, after standing if very dilute) a *reddish-brown precipitate of palladous bromide*, PdBr$_2$.

5. Hydrobromic acid and bromides are oxidised by many oxidising agents with the liberation of bromine. Thus, **nitric acid** *decomposes* hydrobromic acid and the bromides (with the exception of silver bromide) *when heated*, and *liberates bromine*. In the case of a solution the bromine colours it yellow or reddish-yellow; if the bromide was present in solid form or in concentrated solution, brownish-red, or, if dilute, brownish-yellow bromine vapours escape simultaneously, which vapours, if in sufficient quantity, condense to small drops in the cooler parts of the test-tube. In very dilute solutions of bromides bromine is not liberated *in the cold*, either by *nitric acid*, even red fuming acid, or by a solution of *nitrous acid* in *concentrated sulphuric acid*, or by *hydrochloric acid* and *potassium nitrite* (free from nitrate).

6. **Chlorine gas** or **chlorine water** *immediately liberates bromine* in solutions of bromides, *whereby the liquid becomes yellowish-red* if the quantity of bromine is not too small. A large excess of chlorine should be avoided, because it causes the colour to disappear, or nearly so. This is an oxidation process, in which the bromine plays an electropositive part. Until recently it was assumed that bromine chloride was formed. The researches of Lebeau and von Karsten have proved, however, that this compound does not exist (*cf.* Abegg, *Handb. anorg. Chem.*, **4**, 2, 295). This reaction is *much more sensitive* if a liquid is added which can absorb the bromine when shaken, and which does not mix with water, especially *carbon bisulphide* or *chloroform*. The neutral or slightly acid solution should be treated in a test-tube with a small quantity of one of the liquids mentioned, so that a *large drop* forms at the bottom, and then *dilute chlorine water added, drop by drop, and the whole shaken.* In the case of any

material proportion of bromine (*e.g.* 1 bromine : 1000 water) the *carbon bisulphide or chloroform will become reddish-yellow;* in the case of very small quantities (1 bromine : 30,000 water) the colour will be faint yellow,[1] but still recognisable.

Ether, which was formerly used, is far less suitable for this reaction. *A large excess of chlorine water should be avoided in these tests;* the chlorine water should be tested by shaking it with water and a little carbon bisulphide or chloroform to see whether it remains colourless (that is to say, free from bromine). Only when this is the case can the chlorine water be used. On shaking and heating the solution of bromine in carbon bisulphide, chloroform (or ether), with a little alkali hydroxide solution, potassium bromide and potassium bromate will be formed in the solution, and consequently the yellow colour will disappear. On evaporating the solution and igniting the residue the potassium bromate is converted into potassium bromide. The ignited mass can then be subjected to further tests according to 7.

7. On heating bromides with **manganese dioxide** or **lead peroxide** and **sulphuric acid** (concentrated or dilute), *brownish-red bromine vapour is liberated.* In the presence of chlorides dilute solutions must be used to avoid the decolorisation mentioned in 6. When heated with manganese dioxide and acetic acid, bromides do not produce bromine, but they do so *when heated with lead peroxide and dilute acetic acid* (Vortmann); also when heated with *potassium permanganate and acetic acid.* In the case of very small quantities of bromide, the colour of the escaping bromine vapour is not visible. If, however, mixtures which produce bromine vapour are heated in a small distillation apparatus, and the vapour passed through a long glass condensing tube, the colour of the bromine vapour will, as a rule, be visible on looking lengthways down the tube; the first drops of the distillate are also of a yellow colour.

8. For the detection of *free bromine* in vapours or solutions, use may be made of the *colour reactions* which it gives with organic substances. Thus, *moist starch turns yellow* on contact with bromine vapour (but this reaction is not very convenient). To detect traces of free bromine, fluorescein paper may be used, the yellow colour of which is turned to pink by bromine vapours, owing to the formation of eosin. To prepare the paper, strips of paper are soaked with a solution of fluorescein in 40 to 50 per cent. acetic acid, dried and slightly moistened again before use. Fluorescein paper

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[1] The reaction does not take place in hydrobromic acid solutions containing alkaloids, owing to the formation of bromination products. The alkaloids should be removed, therefore, by sodium hydroxide or carbonate, etc. (A. Weller, *Zeitsch. anal. Chem.*, **26**, 740).

keeps better if it is prepared with a 0·04 per cent. alcoholic fluorescein solution, which has been treated with 2 or 3 drops of ammonia solution. Bromine may be detected in the presence of chlorine by the fact that the colourless paper is turned red by ammonia vapour; this colour does not disappear even on contact with acetic acid vapour. Ammonia vapour also produces a faint red coloration in the presence of chlorine alone, but this disappears in the air, and especially on contact with acetic acid vapour. In the case of mixtures of solid salts, the bromine can be liberated by means of red lead and acetic acid (D. Ganassini, *Chem. Zentr.*, 1904, I., 1172). If much free chlorine is present in addition to a little bromine, no reaction will result; in such a case the halogens must first be converted into bromide and chloride, and the bromine liberated from the mixture of salts by means of a suitable oxidising agent (a saturated cupric sulphate solution treated with permanganate without heating). The reaction may be carried out in a test-tube, or in the case of more delicate tests in a distillation flask, into which a current of air is introduced, and into the outlet tube of which a piece of moistened fluorescein paper is inserted. Iodides, if present, have no disturbing influence if they are first converted into iodate by heating them with permanganate (H. Baubigny and P. Rivals, *Chem. Zentr.*, 1904, I., 212).

On treating a *magenta solution*, previously *reduced* by means of sodium hydrosulphite and hydrochloric acid, with a few drops of bromine water, a deep bluish-violet coloration is produced; iodine water produces no coloration; with chlorine water the colour is yellowish-brown and occasionally red. This reaction is also suitable for the detection of bromine in the presence of iodine and chlorine; it is very sensitive and is particularly sharp if paper saturated with the reagent is exposed to bromine vapour. To detect alkali bromide in the presence of chloride and iodide, the mixture of salts should be dissolved in a little water in a small flask or beaker, treated with a few cubic centimetres of a 15 to 25 per cent. chromic acid solution, and the paper moistened with the reagent exposed to the resulting vapour. Other dyestuffs also give characteristic reactions; thus, a solution of *Hofmann's violet* decolorised by means of a hydrogen sulphite and hydrochloric acid is coloured deep blue by bromine, the reaction occuring also in the presence of iodine and chlorine. If the reaction is to be used for the detection of bromine ion in the presence of cyanogen, ferrocyanogen, ferricyanogen or thiocyanogen ions, the bromine must be liberated by means of chromic acid (J. Guareschi, *Zeitsch. anal. Chem.*, **52**, 451, 538, 607; **53**, 490).

9. On pouring *concentrated sulphuric acid* on to a mixture of *bromide and potassium dichromate* and heating it, *pure bromine* will be produced, but *no chromium compound*, as in the case of chlorides; the liquid which distils, therefore, becomes *colourless and not yellow* when treated with ammonia solution in excess. Bromine may also be removed from solutions when heated with potassium dichromate

and sulphuric acid ; on the other hand, bromine is not liberated from solutions in the cold or with dilute sulphuric acid.

10. On treating a solution of hydrogen bromide or the solution of an alkali bromide with a little *auric chloride solution*, *a straw-coloured to dark orange-red coloration* will appear, owing to the formation of auric bromide. If an iodine compound is present it must be removed before proceeding with the reaction (Bill).

11. For the detection of bromine ion in *metal bromides insoluble* in water and nitric acid, the salts should be treated in the same way as the corresponding metal chlorides ; in the case of non-electrolytes containing bromine and organic bromo-substitution products, the instructions given in Sec. 117, 10, in connection with chlorine, should be followed.

12. A **bead of alkali phosphate** saturated with **cupric oxide** and treated with a substance containing bromine, when ignited in the inner gas or *blowpipe flame*, *gives the flame a blue colour bordering on green*, especially at the edges (Berzelius).

13. With regard to the *microchemical detection* of bromine ion, see Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 174 ; A. Percy Smith, *Pharm. Zentralh.*, **27**, 638 ; E. Pozzi-Escot, *Chem. Zentr.*, 1907, II., 1355.

SEC. 119.

(c) **Hydriodic acid,** HI (Iodine ion, I′).

1. *Iodine* is a solid, soft substance, as a rule lustrous, usually crystallising in tablets, and having a characteristic unpleasant odour. It melts at 114°, boils at over 200°, and gives off violet iodine vapour, which, on cooling, condenses to a black sublimate ; it volatilises very appreciably at the ordinary temperature, and is also volatile with steam. It dissolves but slightly in water (the solution is light brown), but easily in alcohol, ether, carbon bisulphide, chloroform, and also in aqueous potassium iodide solution, and in hydriodic acid. The solutions in alcohol, ether, hydriodic acid, and potassium iodide solution are a dark reddish-brown, those in carbon bisulphide and chloroform are violet-red. Iodine bleaches vegetable colouring matters slowly and slightly ; its vapour turns moistened red litmus paper lavender-blue ; it colours the skin brown ; with **starch** it forms *an extremely intense dark blue compound* or colloidal solution. This is always produced when iodine vapour or a solution containing free iodine is brought into contact with starch, preferably *starch*

paste.[1] It is decomposed by alkali hydroxide, chlorine, and bromine, as well as by sulphur dioxide and other reducing agents.

2. *Hydrogen iodide*, HI, is a gas similar to hydrogen chloride and hydrogen bromide, and soluble to a considerable extent in water. The colourless *aqueous hydriodic acid* rapidly turns reddish-brown when in contact with the air, whilst water and a solution of iodine in hydriodic acid are formed. Hydriodic acid is also a strong acid, and in this respect its behaviour is analogous to that of the two other halogen acids.

3. The *iodides*, too, correspond in many respects to the chlorides. A great number of the iodides of heavy metals are, however, insoluble in water. Many, as, for instance, lead iodide, mercurous and mercuric iodides, have characteristic colours.

4. **Silver nitrate** produces in aqueous solutions of hydrogen iodide and the iodides yellowish-white precipitates of *silver iodide*, AgI, which turn black in the light. This precipitate is insoluble in dilute nitric acid, scarcely soluble in 5 per cent. ammonia solution, and is insoluble in a boiling solution of ammonium sesquicarbonate[2] (H. Hager), but is readily soluble in solutions of potassium cyanide and concentrated sodium thiosulphate.

5. *Palladous chloride* and *palladous nitrate* produce even in very dilute solutions of hydriodic acid or of an iodide a *brownish-black precipitate of palladous iodide*, PdI_2, which dissolves in an excess of potassium iodide solution and in ammonia solution, is slightly soluble in salt solutions (sodium and magnesium chloride, etc.), and not soluble, or scarcely so, in cold hydrochloric and nitric acids.

6. A solution of 1 part of **cupric sulphate** and 2.5 parts of ferrous sulphate precipitates *cuprous iodide*, Cu_2I_2, from aqueous neutral solutions of iodides, in the form of a *dirty white precipitate*. The addition of a little ammonia promotes the complete precipitation of the iodine ion. Chlorides and bromides are not precipitated by this reagent. In its stead, a solution of *cupric sulphate* may be used, which has been previously treated with *sulphur dioxide* or *sodium hydrosulphite* or other reducing agent (*cf.* Sec. 75, 11) in sufficient excess. The cuprous iodide precipitate is produced without the use of a reducing agent, but its colour is masked by the liberated iodine.

7. *Mercurous chloride, when shaken* with a sufficiently dilute

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[1] This is prepared by finely triturating starch with cold water, and pouring this turbid liquid while continually stirring it, in a thin stream into boiling water (in all 1 part of starch to about 100 parts of water); this is boiled for a short time, allowed to subside, and the almost clear solution used.

[2] *Cf.* footnote, p. 446

solution of iodides, *causes the separation of yellow mercurous iodide*, Hg_2I_2. The reaction is very sensitive, and is also obtained with *mercurous bromide*. (White mercurous bromide is separated from bromide solutions by means of mercurous chloride. O. Wentzki.)

8. On treating a solution of an alkali iodide with *ammonia* and a little *potassium hydroxide*, and adding a few drops of *mercuric chloride solution*, a reddish-brown precipitate of dimercuric ammonium iodide is produced (*cf.* Sec. 30, 10). This is a very sensitive reaction (G. Denigès).

9. Pure *nitric acid*, free from nitrous acid, *decomposes* hydriodic acid or iodides *only when it is in concentrated condition, especially when heated*. **Nitrous acid** or **hyponitric acid,** on the other hand, *decomposes the iodine compounds already mentioned very easily*, even when they are contained in exceedingly dilute solution. *Colourless solutions of iodides therefore turn brownish-red immediately* when a little **red fuming nitric acid** or a mixture of it in concentrated sulphuric acid, or better, a **solution of nitrous acid in concentrated sulphuric acid,** or **potassium nitrite** with a little **sulphuric** or **hydrochloric acid,** is added. *If the solutions are at all concentrated the iodine separates in black flakes*, while iodine vapour and nitric oxide escape.[1]

10. As the *blue coloration of the starch iodide* is visible in much greater dilution than the yellow coloration of the solution of iodine in water, *the sensitiveness of the reaction, which depends on the separation of free iodine*, is considerably increased, when the liquid to be tested for iodine ion is first treated with a little thin, fairly clear **starch paste** (see footnote to 1), then a few drops of dilute sulphuric acid added, so that the liquid becomes strongly acid and, finally, one of the reagents mentioned in 9 added. In order to give a particularly sharp reaction, *one drop* of the solution of *nitrous acid in concentrated sulphuric acid* only need be added (on a glass rod), so that this reagent, first suggested by Fr. J. Otto, may be strongly recommended. If red fuming nitric acid is used, a little more must be added to bring the reaction to the highest degree of intensity, for which reason it is not very suitable for the detection of very small quantities of iodine.

Potassium nitrite also gives a particularly sensitive reaction. The liquid under examination should be treated with dilute *sulphuric acid* or with *hydrochloric acid until the reaction is distinctly acid*, and

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[1] Iodine is not separated from cyanogen iodide by oxidising agents, but a separation is produced by reducing agents (E. v. Meyer, *Zeitsch. anal. Chem.*, **27**, 229).

one or two drops of a concentrated solution of *potassium nitrite* added. In the case of very small quantities of iodine, the liquid turns red instead of blue. An excess of liquids containing nitrous acid does not materially influence the reaction. *As starch iodide yields with hot water a colourless solution, the liquids must necessarily be cold.* The colder they are the more sensitive is the reaction. If it is a question of attaining the highest degree of sensitiveness, the liquid should be cooled with ice, the starch allowed to subside, and the result observed by placing the test-tube on white paper (*cf.* also *Summary and Remarks*, Sec. 125, 6).

11. **Chlorine gas** and **chlorine water** *also convert iodine ion into the elementary condition, but an excess of chlorine combines with it to form iodine chloride*, or oxidises it (finally to iodate ion). *Hence a dilute solution of an iodide, to which starch paste has been added, turns blue immediately on the addition of a little chlorine water, but is decolorised again if more chlorine water is added.* As it is therefore difficult not to overstep the dividing line, especially in the case of very small quantities of iodine, chlorine water is less suitable for their detection.

12 If a solution containing hydriodic acid or an iodide (if necessary acidified) is treated with **carbon bisulphide** or *chloroform, so that a large drop remains undissolved, a reagent which will liberate iodine added* (a drop of a solution of nitrous acid in concentrated sulphuric acid, hydrochloric acid and potassium nitrite, chlorine water, *an excess of which must be avoided*, etc.), *the whole well shaken and allowed to stand*, the carbon bisulphide or chloroform will subside and be *coloured dark or light violet-red* by the absorbed iodine. *This also is an exceedingly sensitive reaction.* On shaking a solution containing free iodine with *petroleum spirit*, *benzene*, or *ether*, the two former are just coloured *red*, and the ether *reddish-brown* or *yellow*. (Iodine gives ether a more intense colour than does an equal quantity of bromine.)

13. Hydriodic acid and iodides are decomposed by numerous other *oxidising agents*, by *potassium dichromate* in the presence of *dilute sulphuric acid*, even in the cold (distinction from bromine), by *persulphates*, and by *hydrogen peroxide* or *potassium permanganate* and *acetic acid*; iodine is also separated when iodides are heated with *manganese dioxide* or *lead peroxide*, with *dilute sulphuric* or *acetic acid*, with *cupric chloride*, *ferric chloride*, or *ferric sulphate*, and may be recognised by the colour of its vapour and, when in small quantities, better by its action on paper moistened with starch paste. If iodides

are heated with *concentrated sulphuric acid*, hydrogen iodide and products of the reduction of sulphuric acid (sulphur dioxide or hydrogen sulphide) are formed as well as free iodine.

14. When fused with *alkali carbonate* (preferably sodium potassium carbonate), the *iodides insoluble* in water and nitric acid behave in a similar manner to the corresponding chlorides. Non-electrolytes and organic iodine products of substitution should be treated according to the instructions given in connection with chlorine (Sec. 117, 10).

15. When a **bead of alkali phosphate** is saturated with **cupric oxide,** treated with a substance containing iodide, and ignited in the inner *gas or blowpipe flame*, it will impart an intense green colour to the flame.

16. With regard to the *microchemical detection* of iodine, see Haushofer, *Mikroskopische Reaktionen*, p. 52; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 176; Denigès, *Zeitsch. anal. Chem.*, **34**, 611.

SEC. 120.

(d) **Hydrocyanic acid,** HCN (Cyanogen ion, CN′).

1. *Cyanogen*, C_2N_2, is a colourless gas of sp gr. 1 8, fairly soluble in water, having a characteristic and penetrating odour, and burning with a carmine-red flame. The aqueous solution produces with hydrogen sulphide a red crystalline precipitate of the amide of thio-oxalic acid, $(CSNH_2)_2$. Cyanogen acts on alkali hydroxides in an analogous manner to the halogens, and forms cyanogen ion and cyanate ion.

2. *Hydrocyanic acid* (prussic acid), HCN, is a colourless, volatile, inflammable, *highly poisonous* liquid with a heavy odour of bitter almonds; it can be mixed with water in all proportions, and in the pure condition soon decomposes. Hydrocyanic acid is a very weak acid (dissociation constant at $18° = 4.7.10^{-10}$), it is scarcely dissociated in its solutions, in 0·1 *N*-solutions, for example, only to 0·006 per cent., and its aqueous solution, therefore, does not redden litmus paper.

3. Of the *cyanides* those of the alkali metals and the alkaline earth metals are soluble in water; the solutions are dissociated into hydroxide and hydrocyanic acid by hydrolysis, and therefore give an alkaline reaction and have the odour of hydrocyanic acid. They are easily decomposed by acids, even by carbon dioxide. At 50° to 80° mercuric cyanide, and at 100° cyanides insoluble in water, but

finely distributed therein, are also decomposed by carbon dioxide (A. Hilger and K. Tamba). Potassium and sodium cyanide melt when ignited in the absence of air, without decomposition; in the presence of air they absorb oxygen; when fused with lead, copper, antimony, and stannic oxides, and many other oxides, they reduce these, and are themselves converted into cyanates; on fusion with nearly all metal sulphides alkali thiocyanates are formed. Of the cyanides of the heavy metals only mercuric and auric cyanide are soluble in water; they are all decomposed on ignition either, like the cyanides of the "noble" metals, into gaseous cyanogen (which escapes) and metal, whereby, owing to the partial polymerisation of the cyanogen to paracyanogen, $(CN)_x$, a mixture of the metal with solid black paracyanogen may remain as residue; or, like those of the other heavy metals, into nitrogen and metal carbide. Many cyanides of the heavy metals are not decomposed by dilute oxygenated acids, and only with difficulty by concentrated nitric acid. All cyanides are decomposed on being heated and evaporated with concentrated sulphuric acid, in which process carbon monoxide and ammonia or ammonium sulphate, as well as the sulphates of the metals are formed; some cyanides are decomposed by hydrochloric acid, and many by hydrogen sulphide.

4. The cyanides have a great tendency to combine with one another, and most cyanides of the heavy metals, therefore, dissolve in potassium cyanide solution. The resulting compounds are *complex salts*, which contain a complex anion consisting of cyanogen and a heavy metal (iron, cobalt, manganese, chromium).[1] Many of these salts are decomposed by dilute acids in such a way that hydrogen cyanide and the salts of the two metals present with the added acids are formed, and others in such a way that hydrocyanic acid, the alkali salt of the added acid and the heavy metal cyanide, stable towards acids (as a precipitate), are formed. A third group contains complex anions which are so stable that they remain unchanged even on the addition of another acid, and sometimes liberate the free acids corresponding to the complex anion. Compounds of the latter description are, *e.g.* potassium ferrocyanide, $K_4Fe(CN)_6$, and potassium ferricyanide, $K_3Fe(CN)_6$. Dilute acids do not precipitate metal cyanides in the cold from their solutions. On replacing the potassium by hydrogen, specific acids are formed, which must not be confused with hydrocyanic acid. Their reactions are described in the two following sections.

[1] *Cf.* p. 10.

5. **Silver nitrate** *in excess produces*, in solutions of free hydrocyanic acid and alkali cyanides, *white precipitates of silver cyanide*, $AgCN$, or $[Ag(CN)_2]Ag$, *which dissolve readily in potassium cyanide and sodium thiosulphate solutions, more sparingly in ammonia solution, and not at all in dilute nitric acid;* they are *decomposed on ignition*, and *leave a residue of metallic silver* and a little paracyanogen. The sensitiveness of the reaction is increased in the presence of free hydrocyanic acid if the solutions are first treated with an excess of ammonia, then with silver nitrate solution, and finally acidified with nitric acid.

6. **Mercurous nitrate** produces in solutions of the alkali cyanides a *grey precipitate of metallic mercury, whilst the cyanogen ion combines with mercury ion to form soluble, slightly dissociated mercuric cyanide*. (Distinction from chlorine, bromine, and iodine ions.)

7. *On adding to a solution of free hydrocyanic acid first* **ferrous sulphate solution**, to which a drop of **ferric chloride solution** has previously been added, and then a few drops of *alkali hydroxide solution*, until the liquid begins to show an alkaline reaction, *a bluish-green precipitate is formed*. If this is acidified with hydrochloric acid, the ferro-ferric hydroxide dissolves, whilst Prussian blue remains undissolved (*cf.* p. 251, 8).[1] The reaction proceeds in such a way that first of all from ferrous ion and cyanogen ion ferrocyanogen ion is produced, which, in acid solution, combines with ferric ion to form Prussian blue. In the case of very small quantities, the liquid becomes green after the addition of hydrochloric acid, and only after standing for some time is a slight blue precipitate obtained. Heat promotes the precipitation, but an excess of alkali hydroxide or hydrochloric acid must be avoided. Similar phenomena with corresponding results occur when a ferrous sulphate solution containing ferric sulphate or ferric chloride is added to a solution of alkali cyanide, with the subsequent addition of hydrochloric acid after the liquid has been allowed to stand. Substances which do not give the Prussian blue reaction without treatment should be heated with dilute sulphuric acid in a test-tube, and the mouth closed with a piece of filter paper, the centre of which has been moistened with a few drops of an alkali hydroxide solution. The hydrocyanic acid which is evolved in the presence of cyanides is absorbed by the alkali. The portion of paper which is being treated should be lightly touched

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[1] Attention may be called to the fact that, even in the absence of cyanogen ion, a bluish-green precipitate of ferro-ferric hydroxide is produced by alkali hydroxide. This, however, dissolves to a clear solution in hydrochloric acid.

with very dilute ferrous sulphate solution, exposed to the air for a short time, and finally treated with steam. If the spot is now touched with hydrochloric acid it will show a Prussian blue coloration if cyanide was present (G. Lockemann).

8. *On mixing a liquid containing hydrocyanic acid or alkali cyanide* (after adding a drop of dilute alkali hydroxide solution, if free hydrocyanic acid is present) *with sufficient* **yellow ammonium sulphide** (containing polysulphide) *to colour the liquid yellow, heating it in a porcelain dish on the water bath* until the mixture is decolorised and the excess of ammonium sulphide is evaporated or decomposed, and then evaporating it to dryness, the residue will contain *alkali thiocyanate.* This is dissolved in a little water, acidified with 2 or 3 drops of *hydrochloric acid*, allowed to stand for a few minutes in order to destroy the thiosulphates formed, which would reduce the ferric salt and thus prevent the reaction, and finally treated with a little ferric chloride. *The resulting thiocyanogen ion may be recognised by its blood-red colour.* If a violet coloration appears or the red one rapidly disappears, a little more ferric chloride must be added to produce the reaction (Liebig, Almén). This reaction is exceedingly sensitive, $(NH_4)_2S_2+KCN=KCNS+(NH_4)_2S$. If an acetate is present, the reaction will only occur on the addition of more hydrochloric acid.[1] In the case of substances to which the reaction is not directly applicable, the same course may be adopted as described in connection with the Prussian blue reaction (7), but the filter paper must be soaked with a few drops of ammonium sulphide, as well as with alkali hydroxide solution. If cyanogen ion is to be detected in insoluble compounds by converting it into ferric thiocyanate, sodium thiosulphate is fused on a loop of platinum wire in a spirit flame until the water of crystallisation has escaped and the mass swells up. A small portion of the substance is then added, the mixture heated for a short time in the flame, removed as soon as the sulphur begins to burn, and the mass on the loop dipped into a few drops of ferric chloride solution, which has been diluted and treated with a little hydrochloric acid. If cyanogen ion was present, the blood-red coloration of ferric thiocyanate will be produced, and not disappear on standing. If the mixture is heated for too long a time the reaction will fail, because the sodium thiocyanate formed will be

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[1] According to Lavialle and Varenne, *Zeitsch. anal. Chem.*, **56**, **128**, meconic acid interferes with the reaction, as it also produces a red coloration. Auric chloride destroys the coloration produced by hydrocyanic acid, but not that produced by meconic acid.

decomposed again. This method is particularly suitable for the distinction of silver cyanide from silver chloride, bromide, or iodide (A. Fröhde).

9. *On treating a liquid containing hydrogen cyanide or the solution of an alkali cyanide with a few drops of a solution of* **alkali nitrate,** adding two to three drops of **ferric chloride solution** and sufficient dilute **sulphuric acid** to change the brown colour of the ferric salt first formed just to pale yellow, heating the mixture until it begins to boil, cooling it, treating it with a little ammonia to precipitate the excess of ferric ion, filtering the liquid and adding to the filtrate, which still contains free ammonia, one or two drops of **hydrogen sulphide water,** the solution will show a violet coloration, owing to the action of the hydrogen sulphide upon the *nitroprusside ion* which has been formed (*cf.* Sec. 124, 5 (G. Vortmann)).

10. On treating a moderately concentrated solution of an *alkali cyanide* with a little *picric acid solution* [1] (one part of picric acid and 250 parts of water) and boiling it, the liquid will turn dark red, owing to the resulting *potassium picrocyaminate* (potassium isopurpurate), the colour becoming more intense on standing. If the solution of alkali cyanide is very dilute, only sufficient picric acid should be added to give the liquid a faint yellow colour. After boiling, the red coloration will appear, perhaps not immediately, but on cooling and standing for some time. This reaction, suggested by C. D. Braun, is not so sensitive as those described in 7, 8, and 9, but may be used for the detection of alkali cyanide in the presence of ferrocyanide, which on similar treatment does not yield potassium picrocyaminate. Other reducing substances also give similar colorations when heated with picric acid (J. Anderson, *Zeitsch. anal. Chem.*, **55**, 465).

11. If filter paper is soaked with freshly prepared alcoholic *guaiacum tincture* containing 3 to 4 per cent. of the resin, moistened after evaporation of the alcohol with 0.25 per cent. *cupric sulphate* solution, and exposed to air which contains only a trace of hydrocyanic acid vapour, the paper will turn blue, owing to the action of the ozone formed by the partial reduction of the cupric ion:

$$9CuSO_4+12HCN+3H_2O=[3Cu_2(CN)_2+3Cu(CN)_2]^{2}+9H_2SO_4+O_3$$

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[1] For the detection of free cyanogen in air or illuminating gas, H. Kunz-Krause recommends a mixture of 4 c.c. of a cold saturated aqueous picric acid solution (1 : 86) with 18 c.c. of alcohol and 5 c.c. of 15 per cent. aqueous potassium hydroxide solution, or the reaction described in 11 (*Zeitsch. angew. Chem.*, **14**, **652**).

[2] Probably as a complex compound, $[Cu_2.Cu(CN)_4]$.

(Pagenstecher, Schönbein).[1] The reaction is exceedingly sensitive, and is intensified when the paper is moistened with formaldehyde solution (J. C. Brünnich). H. Kunz-Krause[2] recommends the use of a 3 per cent. alcoholic solution of *pure guaiaconic acid* and a *copper sulphate solution* of 1 : 1000 to render the reaction more sensitive ; the latter is, however, not necessarily decisive for hydrocyanic acid, as guaiacum copper paper is also rendered blue by air containing ammonia, nitrogen trioxide vapours, ozone, bromine, iodine, and chlorine monoxide. It is still less decisive, if it is produced in solutions, since a mixture of guaiacum tincture with very dilute cupric sulphate solution is not only rendered blue by hydrocyanic acid and cyanides, but also by soluble *chlorine, bromine, iodine, and fluorine compounds*, etc. Potassium iodide starch paper moistened with cupric sulphate solution is also immediately turned blue.

12. *Other organic compounds* behave like guaiacum tincture in producing *characteristic colorations in dilute cupric salt solutions in the presence of hydrocyanic acid. Hydrocœrulignone*, a tetrahydroxy-diphenyl derivative, produces in a dilute acetic acid solution of an alkali cyanide (treated with a little *cupric acetate*) a *crystalline, purple precipitate of cœrulignone ;* in the case of very dilute solutions *the colour is brick-red.* Similar reactions are given by other substituted tetradiphenyl derivatives (J. Moir). On treating a *cupric acetate solution* with a few drops of an alkali cyanide solution and adding *benzidine acetate*, a *dark blue precipitate* is formed. Iodides and bromides behave in a similar manner, and various oxidising agents, such as chromates, ferricyanides, ferric chloride, and others give a blue precipitate with benzidine alone. The reaction is, however, characteristic of cyanogen ion, if carried out with the addition of *disodium hydrogen phosphate*, and if no great quantity of thiocyanate is present. In the presence of thiocyanate the substance is boiled with sodium carbonate solution, and a current of carbon dioxide passed through the filtered solution. This liberates hydrocyanic acid and carries it away. It is conducted into the reagent, which consists of 1 drop of 3 per cent. cupric acetate solution, 5 drops of saturated benzidine acetate solution, and 0·5 c.c. of water (C. Pertusi and E. Gastaldi, *Zeitsch. anal. Chem.*, **53**, 387).

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[1] *Cf.* also the communications of Ed. Schaer (*Arch. d. Pharm.*, **238**, 42, 179 ; **239**, 610 ; **241**, 401), where he recommends that the solutions to be tested for hydrogen cyanide should be shaken with a ½ to 1 per cent. solution of pure guaiaconic acid in chloroform ; he also gives various other reactions for cyanogen compounds.

[2] *J. Gasbeleucht.*, 1901, 726 ; *Zeitsch. anal. Chem.*, **55**, 467.

13. ***On treating a very dilute starch iodide solution with a trace*** ***hydrocyanic acid,*** or, after the addition of a little dilute sulphuri acid, with a trace of an alkali cyanide, *the colour disappears immediately* or after a short time, because the iodine reacts with the hydrocyanic acid to form cyanogen iodide and hydrogen iodide (Schönbein This is a very sensitive reaction, which, however, is never decisiv by itself, as many other substances decolorise starch iodide.

14. Cyanogen cannot be detected in *mercuric cyanide* by th reactions described, with the exception of the thiocyanate reaction (8 In order to detect it in mercuric cyanide, the solution of the sal should be treated with *hydrogen sulphide*, whereby a precipitate o mercuric sulphide is obtained, whilst free hydrocyanic acid remain in solution. Mercuric cyanide is also decomposed by *powdere magnesium* or *antimony*. The hydrogen cyanide formed may b distilled in a current of carbon dioxide, received in water, and identified therein by one of the above-mentioned reactions (Pertusi *Chem. Zentr.*, 1915, I, 7). Solid mercuric cyanide is most easil recognised when heated in a glass tube (*cf.* 3). On heating a mercuri cyanide solution with *hydrochloric acid* or with *sodium chlorid* and *oxalic acid*, or with *sodium chloride* and *dilute sulphuric acid* in a distillation apparatus, the greater portion of the cyanogen ion will be found in the distillate as hydrogen cyanide. In the case of small quantities it is best distilled with tartaric acid and a little hydrogen sulphide water (Autenrieth).

15. With regard to the *microchemical detection* of hydrogen cyanide, see Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 180.[1]

SEC. 121.

(e) Hydroferrocyanic acid, $H_6Fe(CN)_6$ (Ferrocyanogen ion, $Fe(CN)_4''''$).[2]

1. *Hydroferrocyanic acid* is colourless, crystalline, and easily soluble in water. The solution gives a strongly acid reaction Some of the ferrocyanides are soluble in water, such as those of th alkali and alkaline earth metals,[3] but the greater number ar insoluble. They are all decomposed on ignition; if they are no completely dehydrated, hydrocyanic acid, carbon dioxide, and

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[1] With regard to the detection of cyanogen in flames, *cf.* C. Lüdeking *Zeitsch. anal. Chem.*, **29**, 312.

[2] With regard to its constitution, *cf.* p. 10.

[3] Some of the double ferrocyanides of the alkali and alkaline earth metal are, however, insoluble, *e.g.* calcium ferrocyanide, see Sec. 36, 7; and Sec. **34**, **10**.

ammonia escape; if free from water, nitrogen, and occasionally cyanogen, escape.

2. **Ferric chloride** produces in aqueous solution of hydroferrocyanic acid or of the ferrocyanides a blue precipitate of *ferriferrocyanide* (Prussian blue), $Fe_4[Fe(CN)_6]_3$ (*cf.* Sec. 62, 8). **Cupric sulphate** gives a brownish-red precipitate of *cupric ferrocyanide*, $Cu_2Fe(CN)_6$ (*cf.* Sec. 75, 10). **Silver nitrate** precipitates *silver ferrocyanide*, $Ag_4Fe(CN)_6$, as a white precipitate, insoluble in nitric acid and in ammonia solution (on short treatment in the cold), but soluble in potassium cyanide solution. When boiled with ammonia solution, silver ferrocyanide yields ferrous hydroxide, whilst the solution contains complexes of silver cyanide and ammonium cyanide (Weith). *Lead acetate* produces a white precipitate not appreciably soluble in dilute nitric acid. *Thorium nitrate* precipitates from dilute acid solutions of ferrocyanides all the ferrocyanogen ion. (Distinction and method of separating ferricyanogen ion, from thiocyanogen ion. Browning and Palmer, *Zeitsch. anal. Chem.*, **50,** 771.)

3. On mixing a not too dilute solution of an alkali ferrocyanide with *hydrochloric acid* and pouring *ether* over the liquid, hydroferrocyanic acid will separate in crystalline form at the point of contact.

4. Alkali ferrocyanides are not decomposed in aqueous solution by *carbon dioxide* in the cold (distinction from alkali cyanides), but are decomposed at a temperature of 72° to 74° (Autenrieth); Prussian blue and cupric ferrocyanide suspended in water are, however, only decomposed at 100°. When boiled with water, soluble, as also finely distributed insoluble ferrocyanides, are decomposed without the co-operation of carbon dioxide, and hydrogen cyanide is formed (A. Hilger and K. Tamba). Solutions of ferrocyanides, rendered alkaline by means of sodium carbonate, yield no hydrocyanic acid when distilled in a *current of carbon dioxide*. Even when distilled with *sodium hydrogen carbonate*, ferrocyanides do not yield hydrogen cyanide (Jacquemin).

5. Ferrocyanides are not decomposed by *cold dilute acids*, or only to a slight extent. On heating they are decomposed, whilst hydrocyanic acid is liberated, and in this way most of the compounds resembling Prussian blue are produced. On heating ferrocyanides with a mixture of 3 parts of concentrated *sulphuric acid* and 1 part of water until the free acid has been expelled, they are decomposed, and the cyanogen is expelled as hydrogen cyanide;

the metals remain as sulphates. Ferrocyanides are decomposed in a similar way when their slightly acidified solutions are heated with 10 per cent. *ammonium persulphate solution.* The liquid should not be boiled, as the reaction would then be too violent (Dittrich and Hassel, *Chem. Zentr.*, 1903, II, 220). Concentrated sulphuric acid decomposes all ferrocyanides when heated, with the evolution of carbon monoxide. When introduced into fused potassium nitrate, carbon dioxide and nitrogen are formed from the cyanogen, the metals being obtained in the fused mass as oxides.

6. Acidified solutions of ferrocyanides are converted by *hydrogen peroxide,* on heating, into ferricyanides (Weltzien).

7. Insoluble ferrocyanides are decomposed on boiling with *sodium hydroxide,* with the separation of the particular hydroxide (in so far as this is not soluble in sodium hydroxide) and the formation of sodium ferrocyanide.

8. On heating *ammoniacal silver solution* with ferrocyanides, *e.g.* Prussian blue, ferric hydroxide separates. The solution then yields a precipitate of silver cyanide when acidified with nitric acid (Weith).

SEC. 122.

(f) **Hydroferricyanic acid,** $H_3Fe(CN)_6$ (Ferricyanogen ion, $Fe(CN)'''_6$).[1]

1. *Hydroferricyanic acid* forms brown needles, and the ferricyanides are also all coloured. Hydroferricyanic acid and the ferricyanides of the alkali metals, alkaline earth metals, and trivalent iron are soluble in water; all ferricyanides undergo a similar decomposition on ignition to that of the ferrocyanides.

2. **Ferric chloride** does *not* produce a *blue precipitate* in aqueous solutions of hydroferricyanic acid and its salts (Sec. 62, 9); **ferrous sulphate,** on the other hand, gives a *blue precipitate of ferrous ferricyanide,* $Fe_3[Fe(CN)_6]_2$ (*cf.* Sec. 61, 10); *cupric sulphate* gives a yellowish-green precipitate of cupric ferricyanide, $Cu_3[Fe(CN)_6]_2$, insoluble in hydrochloric acid; **silver nitrate** gives an *orange-coloured precipitate* of silver ferricyanide, $Ag_3Fe(CN)_6$, insoluble in nitric acid, easily soluble in ammonia and potassium cyanide solutions; *lead acetate* gives no precipitate in neutral solution, but if ammonia is added a reddish-brown precipitate is produced. (Distinction from ferrocyanogen ion.) *Cadmium salt solutions* produce

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[1] With regard to its constitution, *cf.* p. 10.

in dilute acid ferricyanide solutions an *orange-coloured precipitate of cadmium ferricyanide*, $Cd_3[Fe(CN)_6]_2$. (Distinction from and method of separation from thiocyanogen ion. Browing and Palmer, *Zeitsch. anal. Chem.*, **50,** 771).

3. Aqueous solutions of ferricyanides behave in the same way as those of the corresponding ferrocyanides when boiled with water or when treated with carbon dioxide or sodium hydrogen carbonate.

4. **Hydrogen sulphide** decomposes the alkali ferricyanides; alkali ferrocyanides and hydroferrocyanic acid are formed, with the *separation of sulphur;* free hydroferricyanic acid is decomposed in the same manner, as also a solution of potassium ferricyanide.

5. Alkali ferricyanide solutions are reduced to ferrocyanides by means of *hydrogen peroxide*, with the *evolution of oxygen* (Weltzien). Alkali ferricyanide liberates iodine from potassium iodide solution.

6. The insoluble ferricyanides are decomposed when boiled with *sodium hydroxide solution.* The liquid filtered from the separated metal hydroxides will contain either sodium ferricyanide only, or a mixture of sodium ferro- and ferricyanide.

7. On being heated with *ammoniacal silver solution*, ferricyanides are decomposed in the same way as the ferrocyanides. Nitric acid precipitates silver cyanide from the ammoniacal filtrate.

8. The ferricyanides are decomposed, like the ferrocyanides, by the action of cold and hot dilute acids, by concentrated sulphuric acid, by heating them with a mixture of 3 parts of concentrated sulphuric acid and 1 part of water, by heating the acidified solution with ammonium persulphate, and by fusion with potassium nitrate.

SEC. 123.

(g) **Thiocyanic acid** (Sulphocyanic acid), HCNS (Thiocyanogen ion, CNS′).

1. *Thiocyanic acid* is a colourless oily liquid, forming, when cooled, a crystalline mass, melting at +5° and, according to Artus, boiling at 85°. It has a pungent odour, similar to that of acetic acid, dissolves in water and alcohol to form solutions which give acid reactions, is poisonous, and gradually decomposes in concentrated aqueous solution into hydrogen cyanide and yellow crystalline persulphocyanic acid, $C_2N_2S_3H_2$. On treating an aqueous solution of thiocyanic acid (or potassium thiocyanate) with a large quantity of *concentrated hydrochloric acid,* decomposition rapidly takes place. Thiocyanic acid is nearly as strong an acid

as the halogen acids, and accordingly its aqueous solutions undergo pronounced dissociation.

2. Most of the *thiocyanates* are soluble in water. Their neutral aqueous solutions are not decomposed on boiling, or scarcely so. On boiling them with *alkali hydrogen carbonates*, ammonium carbonate is formed, but no hydrogen cyanide. When distilled with dilute sulphuric acid, phosphoric acid, or tartaric acid, a portion of the thiocyanogen ion will be found in the distillate as dilute thiocyanic acid, the remainder being decomposed. When heated with dilute nitric acid, violent decomposition takes place, with the evolution of nitric oxide and carbon dioxide, and the formation of sulphuric acid. When ignited in the presence of air, all thiocyanates are decomposed and yield, according to the nature of the cation, sulphur dioxide, sulphates and cyanates, or nitrogen, cyanogen, carbon bisulphide, and sulphide.

3. Solutions of thiocyanic acid or of the thiocyanates are coloured blood-red by **ferric chloride solution,** acidified with *hydrochloric acid* (Sec. 62, 10).

4. **Cupric sulphate** produces in solutions of alkali thiocyanates, if they are concentrated, a black precipitate of *cupric thiocyanate*, $Cu(CNS)_2$; if they are dilute only an emerald-green coloration is produced. *Cupric sulphate solution* mixed with **sulphur dioxide** in excess [1] gives, even in the case of great dilution, a pale reddish-white precipitate of *cuprous thiocyanate* (Sec. 75, 11).

5. **Silver nitrate** produces a *white caseous precipitate of silver thiocyanate*, AgCNS, insoluble in cold dilute nitric acid, but soluble in ammonia solution.

6. *Mercurous nitrate* produces a grey or white precipitate, according to the proportions and the concentration. The latter precipitate is mercurous thiocyanate, $Hg_2(CNS)_2$.

7. Thiocyanic acid or the acidified solution of thiocyanates when treated with *zinc* yields *hydrogen sulphide*.

SEC. 121.

(h) **Hydrosulphuric acid,** H_2S (Sulphide ion S'', Hydrogen sulphide ion, HS').

1. Sulphur occurs in very different modifications. That which is stable at the ordinary temperature is α-sulphur, a solid, brittle friable, tasteless, yellow substance, insoluble in water, forming

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[1] Or another suitable reducing agent, see Sec. 75, 11.

rhombic crystals and of sp. gr. 2·03 to 2·06. At 114·4° α-sulphur melts to an oily, mobile liquid, from which, on solidification, the monosymmetrical modification, β-sulphur (of sp. gr. 1·975), stable at above 95·6°, crystallises. Above 160° the melted sulphur turns brown, then increasingly becomes more viscous, but at 400° again becomes fluid, and boils at 444·5°. The escaping brownish-yellow vapour condenses in cold air to a yellow powder, and on the sides of the vessels to drops. Heated in the air, sulphur burns with a bluish flame to sulphur dioxide, which may be immediately recognised by its suffocating odour. Concentrated nitric acid, bromine with hydrochloric acid, *aqua regia*, and a mixture of potassium chlorate and hydrochloric acid gradually dissolve sulphur on moderate heating, while they oxidise it to sulphuric acid; boiling sodium hydroxide solution dissolves it to a yellow liquid containing sodium sulphide and sodium thiosulphate; it is insoluble in cold ammonia solution, but dissolves slightly if the solution is warm. Carbon bisulphide, benzene, and petroleum spirit dissolve crystalline sulphur easily, but not the amorphous sulphur, which also occurs in several modifications. Under certain conditions, especially on the decomposition of sulphur compounds in aqueous solutions, colloidal modifications of sulphur are produced, which may cause characteristic colour phenomena (*cf.* 3, footnote). When a hydrogen flame is brought into contact with sulphur (or also with sulphides or sulphates) the inner flame will be of a fine blue colour.

2. *Hydrogen sulphide*, H_2S, at the ordinary temperature and atmospheric pressure, is a colourless poisonous gas (easily recognisable by its odour, recalling that of bad eggs), which is soluble in water and transitorily reddens litmus. When ignited it burns with a blue flame, forming water and sulphur dioxide. Hydrogen sulphide water, the properties of which are described on p. 73, is decomposed by chlorine, bromine, iodine, ferric chloride, permanganic acid, chromic acid, nitrous acid, and other oxidising agents, with the separation of sulphur; oxidation also gradually takes place in the air.

Hydrogen sulphide (corresponding to the halogen acids) is a very weak dibasic acid, with the dissociation constant $0.91.10^{-7}$ (for the first stage); in accordance with the position occupied by sulphur in the periodic system, as the element corresponding to oxygen, a certain analogy, however, exists between hydrogen sulphide and water. Accordingly the compounds of sulphur with metals, the sulphides (*e.g.* K_2S, FeS), or those with metals and hydrogen, the hydrogen sulphides (*e.g.* NaHS), correspond on the one hand with oxides and hydroxides, and on the other with neutral and acid salts. In the same way that oxygen can combine with metals in their different valencies to form different oxides and also peroxides, so can sulphur in combination with a metal form different sulphides (monosulphide and polysulphides). According to the nature of the element which is in combination with the sulphur (*i.e.* whether it is electro-positive or negative), the hydrogen sulphides (like the hydroxides) have a basic or acid character. They are, therefore, also termed sulpho bases and sulpho acids. To the latter belong, apart from hydrogen sulphide, especially the hydrogen sulphides of the members of the sixth analytical group (cations).

3. Of the *sulphides of the metals* only those of the alkali and alkaline earth metals are soluble in water. Like the sulphides of iron, manganese, and zinc, they are decomposed by dilute mineral acids, with the evolution of hydrogen sulphide, which may be easily recognised by its odour and by its action on lead salt solution (see 4). In the presence of the sulphide of a metal of high valency, as, for example, *ferric* sulphide or a polysulphide (such as Na_2S_3), a white precipitate of finely divided sulphur will simultaneously separate, and this may be easily distinguished from other precipitates by its solubility in benzene or petroleum spirit.[1] Some of the sulphides of the metals of the fifth and sixth groups are dissolved by boiling concentrated hydrochloric acid, with the evolution of hydrogen sulphide; others are dissolved, not by hydrochloric acid, but by concentrated boiling nitric acid. The compounds of mercury, gold, and platinum resist both acids more or less, but dissolve in heated *aqua regia*. Hydrogen sulphate ion is formed by the solution of sulphides in nitric acid and *aqua regia*, and, in addition, sulphur generally separates. When heated in a glass tube fused together at the bottom, many sulphides, especially polysulphides, yield a sublimate of sulphur. All sulphides are decomposed on fusion with potassium nitrate and sodium carbonate. Sulphur is found in the aqueous extract of the fused mass as sulphate ion.

4. If hydrogen sulphide, either in solution or in the form of gas, is brought into contact with **silver nitrate** or **lead acetate,** *black precipitates of silver sulphide or lead sulphide are produced;* if

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[1] For the detection of polysulphides of the alkali and alkaline earth metals J. C. Gil recommends that 93 per cent. alcohol should be boiled in a small flask and the solution under examination be added when the alcohol vapours have expelled the air. In the presence of polysulphide, the liquid temporarily assumes a faint pale blue coloration, which changes to a permanent greenish-blue

therefore, the odour is not a sufficient means of detecting the hydrogen sulphide, these reagents afford the surest proof of its presence. If it is in the form of gas, and a strip of paper moistened with a lead acetate solution and a little ammonia solution is introduced into the air under examination, the paper indicates the presence of hydrogen sulphide by becoming covered with a brownish-black lustrous film of lead sulphide. If it is a question of detecting a trace of alkali sulphide in the presence of alkali hydroxide or carbonate, the liquid is best mixed with a solution of sodium plumbate, which is prepared by treating lead acetate solution with sodium hydroxide solution until the precipitate has re-dissolved.

5. On treating a liquid containing hydrogen sulphide or alkali sulphide with **sodium hydroxide** and then with **sodium nitroprusside,** $Na_2Fe(NO)(CN)_5+2H_2O$, *the liquid becomes reddish-violet*. The reaction is very sensitive, but in this respect is exceeded by that with sodium plumbate (see 1)[1] A strip of filter paper, saturated with an ammoniacal solution of sodium nitroprusside, may be used for the detection of gaseous hydrogen sulphide (Kràl, Geissler, *Zeitsch. anal. Chem.*, **36**, 696; Scheele, *Ibid.*, **42**, 181).

6. Exceedingly small traces of hydrogen sulphide in aqueous solution may be detected by adding $\frac{1}{20}$ volume of hydrochloric acid and a few grains of *para-aminodimethylaniline sulphate*,[2] and, as soon as the latter has dissolved, one or two drops of a dilute ferric chloride solution. In the presence of hydrogen sulphide *the liquid will become pure blue*, owing to the formation of *methylene blue* (H. Caro, E. Fischer).

7. On adding *mercuric chloride solution*, drop by drop, to a strong hydrochloric acid solution containing but *little* hydrogen sulphide, *a lemon-yellow turbidity* or precipitate will result. (A very sensitive reaction. E. Tiede and F. Fischer, *Ber.*, **44**, 1711.)

8. On heating sulphides in the *oxidation area of a gas or blowpipe flame*, the sulphur contained in them will burn with a blue flame and emit the well-known odour of sulphur dioxide. If sulphides are heated in a glass tube open at each end, held obliquely, and having inserted in its upper end a piece of moist blue litmus paper, the paper will be turned red by the escaping sulphur dioxide. If the products of the combustion are allowed to come into contact

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[1] *Cf.* Virgili, *Chem. Zentr.*, 1906, II., 909.

[2] With regard to the preparation of the reagent, *cf. Zeitsch. anal. Chem.*, 23, 226. Fendler and Stuber recommend, in the place of the reagent in solid form, the use of a 1 per cent. freshly prepared solution (*Zeitsch. Untersuch. Nahr. Genuss.*, **22**, 195).

with the lid of a crucible moistened with an ethereal *phloroglucinol-vanillin solution*, a characteristic red coloration will appear (Raikow, *Zeitsch. anal. Chem.*, **49**, 701). With regard to further reactions for the detection of small quantities of hydrogen sulphide. *Cf.* Curtman, *Zeitsch. anal. Chem.*, **25**, 561; Italie, *Chem. Zentr.*, 1891, II., 498.

9. On boiling a finely powdered sulphide in a porcelain dish with *alkali hydroxide solution, and heating it until the alkali hydroxide begins to fuse*, or on *fusing* the substance with *alkali hydroxide*,[1] then dissolving the mass in a little water, introducing a small piece of bright *silver* (a brightly polished coin), and heating the whole, the metal becomes *brownish-black* owing to the presence of *silver sulphide*. The silver may be made bright again by rubbing it with leather and calcined lime (v. Kobell) [2]

10. If the powder of a sulphide which is not decomposed, or only slightly so, by hydrochloric acid, is mixed in a small cylinder or wide-necked flask with an equal volume of finely ground *iron*, free from sulphur (*ferrum alcoholisatum* of the pharacopœia), and a layer about 1 millimetre high of moderately dilute *hydrochloric acid* poured over it (1 volume of water to 1 volume of concentrated acid), hydrogen sulphide will escape with the hydrogen; the former may be easily recognised if a strip of paper, moistened with lead acetate solution and then dried, is fixed into the neck of the flask by means of a loosely fitting cork, and in such a way that it covers the bottom and sides of the cork. Realgar, orpiment, and molybdenum glance do not give this reaction (v. Kobell).

11. With regard to the *microchemical detection* of sulphur, see Haushofer, *Mikroskopische Reaktionen*, p. 115; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 151; F. Emich, *Zeitsch. anal. Chem.*, **32**, 163; **56**, 101; Schoorl, *Ibid.*, **48**, 675.

SEC. 125.

Summary and Remarks on the Anions of Group II.

1. The anions of the second group are sharply defined from those of the first and third, in that they yield, with silver nitrate, precipitates which are insoluble in dilute nitric acid, whilst those

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[1] With regard to the influence of sulphur contained in illuminating gas, see p. 76, footnote 1.

[2] With regard to a process for the detection of all kinds of sulphur compounds, based on the same principle of conversion into alkali sulphide, *cf.* Deussen, *Zeitsch. anal. Chem.*, **52**, 491.

of the third group do not produce a precipitate with silver nitrate; although those of the first group generally give silver precipitates, yet these re-dissolve in dilute nitric acid, so there can be no question of confusing them with those of the second group.

The different characteristics of the silver compounds of individual members of the second group, as regards their colour and their solubility in ammonia solution, should, in the main, only be used for the purpose of distinguishing between them when not more than one of these anions is present.

2. *Sulphide ion*, which may usually be detected by its odour on being dissolved or acidified, and, in any case, may be recognised by the fact that it gives a black precipitate with silver nitrate, interferes with the detection of the other anions of the second group, and must, therefore, be removed before applying tests for these (*cf.* also 9, p. 178).

If free hydrogen sulphide is present and the solution free from cyanide, the former may be boiled off and may be recognised by its odour during the process or by the tests given in Sec. 121, 4 or 5. Otherwise the sulphide ion may be removed by adding an alkaline zincate solution (zinc sulphate treated with sufficient alkali hydroxide solution to re-dissolve the precipitate first formed), and filtering off the resulting zinc sulphide.

If an insoluble mixture of sulphides with chlorides, bromides, or iodides is present, it should be fused with sodium carbonate and potassium nitrate, and the fused mass treated with carbonic acid water. The solution then contains the sulphur as sulphate ion; also chlorine, bromine, or iodine ion. Bromate and iodate ion may, of course, have been formed as well. In order, therefore, to reduce these to bromine or iodine ion, dilute sulphuric acid and sulphur dioxide or another suitable reducing agent in slight excess should be added.

3. *Ferrocyanogen*, *ferricyanogen*, and *thiocyanogen ions* may be readily recognised by their characteristic reactions with ferrous sulphate or ferric chloride, even in the presence of the other members of the second group. In testing for thiocyanogen ion, however, note should be taken that in the presence of iodide the iodine is liberated by ferric chloride; the iodine dissolves in an excess of alkali iodide solution, giving a red liquid. On the addition, however, of even *one* drop of ferric chloride all risk of a mistake is obviated.

Ferrocyanogen ion may be separated from ferricyanogen, cyanogen, thiocyanogen, chlorine, and bromine ions, but not from iodine ion, by treating the freshly-separated silver precipitate with ammonia, as silver ferrocyanide is insoluble in ammonia solution.

4. *Cyanogen ion* may be recognised in the absence of ferro- and ferricyanogen ions by the Prussian blue reaction with a ferrous-ferric salt; in the absence of thiocyanogen ion by conversion into thiocyanate and treatment with ferric chloride (Sec. 120, 8).[1]

Cyanogen ion may be separated from ferrocyanogen, ferricyanogen, and from thiocyanogen ions (*a*) by treating it with sodium hydrogen carbonate and distilling the liquid (see Part II., Rubric No. (331) 2*a*). Only hydrocyanic acid passes into the distillate. (*b*) Cyanogen ion in the presence of ferrocyanogen, ferricyanogen, and thiocyanogen ions may be detected by adding the solution under examination to an ammoniacal solution of a cupric salt treated with a little hydrogen sulphide. Decolorisation is produced by cyanides, but not by the other ions (Barneby, *Chem. Zentr.*, 1914, II., 435).

The detection of *cyanogen and hydrogen cyanide* present together

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[1] A critical work on the most important reactions of hydrocyanic acid has been published by E. Anderson, *Zeitsch. anal. Chem.*, **55**, 459 We give here the table in which Anderson sets out the result of his experiments on the sensitiveness of the various reactions.

Detection of hydrocyanic acid as	Concentration of the potassium cyanide solution.	Content of CN in 10 c.c. solution.	Capable of detection in dilution of	
			HCN according to test.	HCN as published.
Silver cyanide .	1/10,000 Potassium cyanide	0·00000393	1 : 245,000	1 : 250,000*
Prussian blue . .	1/1,000 Potassium cyanide	0·0000393	1 : 24,500	1 : 50,000*
	1/1,500 Potassium ferrocyanide	0·0000246	1 : 39,100	——
Thiocyanate . .	1/10,000 Potassium cyanide	0·00000393	1 : 245,000	1 : 400,000
With picric acid .	1/100 Potassium cyanide	0·000393	1 : 2,450	1 : 2,000**
Guaiacum tincture	1/100,000 Potassium cyanide	0·000000393	1 : 2,450,000	1 : 300,000

* Link u. Möckel, *Zeitsch. anal. Chem.*, **17**, 455.
** C. Reichardt, *Chem. Zeit.*, **25**, 537.

in gaseous mixtures may, according to Rhodes (*Zeitsch. anal. Chem.*, **53**, 199), be effected by conducting the gas through absorption tubes containing silver nitrate solution, which has been acidified with nitric acid, and then through tubes containing N/2-potassium hydroxide solution free from chloride. In the first absorption vessels hydrocyanic acid is retained and separated as silver cyanide, whilst the cyanogen gas is absorbed by the potassium hydroxide. The resulting potassium cyanide may be recognised by the known methods.

5. The detection of iodine, bromine, and chlorine ions may be interfered with by the presence of cyanogen and thiocyanogen or of complex ions containing cyanogen. Hence, if necessary, these must first be destroyed or removed.

(*a*) This may be done by precipitating all the anions of the second group with silver nitrate after removing the sulphide ion (see 2), and *igniting* the separated and washed *silver precipitate* (apart from the filter) in a porcelain crucible. Whereas silver chloride, silver bromide, and silver iodide do not decompose on fusion, the silver salts of cyanogen and of the complex cyanides are decomposed and leave only silver as a residue, which, in the presence of silver thiocyanate, may contain sulphide. (*α*) By fusing the residue obtained after ignition with *sodium potassium carbonate* (to which a little potassium nitrate is added if thiocyanogen was originally present), and extracting the fused mass with water, there will remain in solution only alkali chloride, bromide, and iodide (possibly also a little alkali sulphate, bromate, iodate, nitrate, and nitrite. See the end of 2). (*β*) Instead of fusing the ignition residue of silver salts with alkali carbonate, it may be reduced with nascent *hydrogen*. It is treated with dilute sulphuric acid, a fragment of zinc added, allowed to stand for some time, and the resulting solution containing chlorine, bromine, and iodine ions, together with zinc ion, filtered. If thiocyanogen was originally present, the solution may be freed from hydrogen sulphide by boiling it, or by rendering it alkaline, and filtering off the zinc sulphide.

(*b*) Cyanogen, ferrocyanogen, and thiocyanogen ions may be removed by precipitation with *cupric sulphate* in the presence of an excess of sulphur dioxide. In this case, however, iodine ion is also precipitated, whilst the filtrate may be tested for chlorine and bromine ions. Bromine may be liberated by potassium permanganate and sulphuric acid (Curtman and Wikoff, *Chem. Zentr.*, 1915, 1., 1280).

6. *Iodine ion* may be recognised easily and with certainty

(*a*) by its reaction with *palladous chloride*, by means of which it may also be separated from bromine ion (Sec. 119, 5, and Sec. 118, 4), and especially (*b*) *by liberating the iodine in its elementary condition, and noting the blue coloration it gives with starch paste*,[1] *or the violet coloration of its solution in carbon bisulphide.*

These two reactions may be interfered with by the presence of cyanogen ion (which in such a case must be removed, as in 5 (*a*)), and by bromine or chlorine. Consequently, if they are present, the iodine must be liberated by such means or under such conditions that the bromine or chlorine is not set free.

The reaction with *carbon bisulphide* may lead to errors in the presence of *thiocyanogen ion*, if nitrous acid is used for the liberation of the iodine, because even in the absence of iodine this may produce a red coloration (Nadler).

The *starch iodide reaction* is influenced by the presence of many salts—alum, magnesium sulphate, alkali sulphate, etc.

The *starch iodide*, as also the *carbon bisulphide reaction*, may be entirely prevented by the presence of many organic substances, *e.g.* by albumin (Puchot), resorcinol, orcinol, and phloroglucinol (Hlasiwetz), tannin, and others. Organic substances must, therefore, be removed before making a test for iodine, *e.g.* by fusion with alkali carbonate and potassium nitrate, or the iodine should be expelled as vapour.

(*c*) *To liberate iodine* nitrous acid dissolved in sulphuric acid, or potassium nitrite and dilute sulphuric acid, or red fuming nitric acid, may be specially recommended (see, however, 6 (*b*), third paragraph, and 7 (*a*), fourth paragraph). Apart from these, many other methods have been proposed, as, for instance, iodic acid or alkali iodate and hydrochloric acid (Liebig), ferric chloride (or ferric sulphate or iron ammonium alum) and sulphuric acid, platinohydrochloric acid and sulphuric acid (Hempel), potassium permanganate, or chromic acid in dilute acid solution, etc.

In this connection we make the following observations:—

Iodic acid should only be used with the greatest care, as on the one hand, iodine may be liberated from the reagent by reducing agents, even in the absence of iodine ion in the substance under examination, and, on the other hand, an excess of iodic acid immediately inhibits the reaction.

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[1] For special details of methods for carrying out this reaction, reference should be made to Morin, *J. prakt. Chem.*, **78**, 1; and Hempel, *Ann. Chem. Pharm.*, **107**, 102.

The ferric compounds do not act immediately in the case of very dilute solutions. If, however, the mixture is allowed to stand for some time the reaction is very sensitive. An excess of the reagent does not matter. This method of liberating iodine is especially to be recommended if the iodine is to be expelled in a gaseous form, *e.g.* in the presence of thiocyanogen ion. or of organic substances which interfere with the identification reactions. In such a case the solution should be heated almost to boiling point and the vapour allowed to come in contact with paper moistened with starch paste.

Ferric salt, free from chloride, may also be used with advantage for the *separation* of iodine from chlorine and bromine ions, the liberated iodine being separated by shaking with carbon bisulphide (see 7 (*b*)).

The reaction with *platinohydrochloric acid* is characterised by the fact that it gives a dark red coloration (see Sec. 31, p. 131).

To detect iodine by means of starch paste in a solution in which it has been liberated with *permanganate*, the reaction should only be noted after six to twelve hours, as otherwise the permanganate coloration may have a disturbing effect.

Permanganate and nitric acid can oxidise all the iodine ion to iodate ion on heating, whilst chlorine ion and bromine ion are converted into volatile compounds (A. F. Seeker and Mathewson, *Zeitsch. anal. Chem.*, 55, 201).

(*d*) *The separation of iodine ion* from chlorine and bromine ions may be effected by treating the precipitated *silver compounds with ammonia*, and more completely by *precipitating the iodine ion as cuprous iodide* (Sec. 119, 6). Iodine ion is best separated from bromine ion alone by means of *palladous chloride*, which only precipitates the iodine ion; it may be separated from chlorine ion by means of *palladous nitrate*, or, after the addition of a sufficient quantity of ammonium sulphate, by *thallous sulphate* (Jannasch and Aschoff).

7. The properties of free bromine, *e.g.* its colour, its odour, and especially the reddish-yellow colour of its solution in carbon bisulphide, are characteristic of *bromine ion*. It is, however, only possible to observe these properties with certainty when iodine or chlorine cannot be simultaneously liberated in the elementary condition. Bromine ion must, therefore, be separated from them if they are present. The iodine may as a rule be detected simultaneously.

(*a*) The iodine is liberated by an agent which has no effect on bromine ion, that is to say, either by the addition of ferric chloride or potassium nitrite or a solution of nitrous acid in concentrated sulphuric acid, or red fuming nitric acid to the liquid, slightly acidified with sulphuric acid. The presence of iodine may be detected by shaking the liquid, with carbon bisulphide, which turns violet, or by means of starch paste, which turns blue.

If chlorine water is gradually added with constant stirring, the iodine reaction is at first intensified, but the colour will then fade, owing to the formation of iodine chloride, and, finally, on the further addition of chlorine water, *bromine* is liberated ; this may be recognised by the fact that on shaking the liquid with carbon bisulphide the latter turns red. An excess of chlorine water should be avoided, as otherwise the bromine coloration will disappear (Sec. 118, 6).

In the presence of much iodine, the liquid, shaken with carbon bisulphide, may be poured through a moist filter instead of converting all the iodine into iodine chloride ; the carbon bisulphide containing the iodine will remain on the filter. The filtrate is now treated with fresh carbon bisulphide and chlorine water added. If all the iodine was previously liberated, the bromine coloration will now appear ; otherwise the carbon bisulphide becomes violet again, and only turns reddish-yellow after the addition of more chlorine water.

If a *chloride* is also present in the solution, and it is a question of *small quantities of iodine ion*, great care must be taken in adding nitrous acid (*one drop* of the nitrite solution is sufficient), so that the iodine reaction does not disappear, owing to the appearance of by-reactions.

(*b*) The iodine may also be expelled by heat, after it has been liberated by sulphuric acid and ferric sulphate (free from chloride), the solution now free from iodine heated with potassium permanganate, and the bromine expelled and conveniently taken up in a little chloroform. The permanganate in the residue may be reduced by means of alcohol, and the test for chlorine ion made with silver nitrate (Hart).

8. *Chlorine ion* may be recognised, in the absence of the other members of the second group, by precipitation with silver nitrate, as well as by its properties in the elementary condition.

In the presence of bromine and iodine ion it may be detected in the following manner :—

(*a*) The solution in which the halogens are present, together with the ions of the alkali or alkaline earth metals, is heated with *dilute* (2 to 3 per cent.) acetic acid and lead peroxide, until the liquid is almost colourless on standing and no longer has the faintest odour of iodine or bromine. In this process all the bromine and a part of the iodine escapes, the rest remaining as lead iodate with the excess of lead peroxide. The liquid is filtered, the precipitate washed with boiling water, and the chlorine ion in the filtrate precipitated with silver nitrate (Vortmann).

If cyanogen ion was also originally present, it is advisable to expel this first, by heating the solution for a sufficient time with acetic acid before the liquid is heated with lead peroxide.

(*b*) *To detect chlorine, bromine, and iodine ions in the presence of one another*, the freshly obtained precipitate of silver chloride, silver bromide, and silver iodide (washed by decantation) is heated with about 80 to 100 times its weight of an aqueous solution of ammonium sesquicarbonate (Sec. 117, 4, p 416, footnote) for 2 or 3 minutes until it boils, the mixture allowed to stand for a short time, decanted, and again boiled with a further quantity of ammonium sesquicarbonate solution. The solution will contain silver chloride (together with a trace of silver bromide). On treating the residue of the silver bromide and silver iodide with 5 per cent. ammonia solution (sp. gr. 0 9783) the silver bromide (with traces of silver iodide) dissolves, whilst almost the whole of the silver iodide is left (Hager). The precipitates from the ammoniacal solutions, and the still undissolved silver iodide, may then be fused separately with sodium carbonate. On treating the fused masses with water, and filtering the liquid, the halogen ions in almost pure condition, as well as sodium ion, will be found in the respective solutions, and further tests may then be made. The detection of chlorine ion is best effected by almost neutralising the liquid with sulphuric acid (the reaction must, however, remain alkaline), evaporating it to dryness, fusing the residue with potassium dichromate, and testing it according to Sec. 117, 8. The following process for detecting small quantities of chlorine ion in the presence of iodine and bromine ions is based on a similar principle. The completely washed silver precipitate is treated for a few minutes in the cold with 1 to 5 times its volume of a 10 to 15 per cent. solution of ammonium sesquicarbonate, allowed to subside, filtered off, and the filtrate treated with *potassium bromide*. The silver ion, which dissolves as silver chloride, and consequently the chlorine ion, may be recognised by the formation of a precipitate. If iodates or cyanides were present, they should first be destroyed (L. L. de Koninck).

(*c*) Chlorine, bromine, and iodine ions in the presence of each other may be recognised by spectroscopic methods (Al. Mitscherlich, *Zeitsch. anal. Chem.*, **4**, 153).[1]

9. A systematic course for the detection of all members of the second group of inorganic anions has been given by H. C. B. Weber and H. A. Winkelmann, *Chem. Zentr.*, 1917, I., 341.

It is based on the following principles: (*a*) The solution is treated with zinc nitrate and nitric acid. The precipitate contains zinc ferro- and ferricyanides. It is filtered off, dissolved by means of sodium hydroxide solution, and treated with ammonia. Zinc ferrocyanide is precipitated, and may be converted into Prussian blue; zinc ferricyanide remains in solution and, on the addition of nitric acid, is precipitated. (*b*) Silver nitrate is added to the filtrate of (*a*); the ions of cyanogen, thiocyanogen, chlorine, bromine, iodine, and sulphide ion are precipitated as silver compounds. (*c*) The precipitate is treated with mercuric acetate, whereby silver cyanide is decomposed. Cyanogen ion then dissolves as mercuric cyanide, and may be detected, *e.g.* by conversion into thiocyanogen ion. (*d*) The residue of (*c*) is treated with sodium formate and sodium hydroxide, silver thiocyanate, and silver chloride being decomposed. Thiocyanogen ion and chlorine ion dissolve as sodium salts. The former is separated as cuprous salt, and the chlorine ion is precipitated with silver nitrate in the filtrate from this. (*e*) The residue of (*d*) is treated with copper and ammonia; bromine and iodine ions dissolve as copper-ammonia compounds. The latter may be separated as cuprous iodide, the former as silver bromide. (*f*) The residue of (*e*), silver sulphide, is oxidised with nitric acid to silver sulphate, and the sulphate precipitated with barium nitrate.[2]

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[1] With regard to the detection of small quantities of chlorine ion in the presence of much iodine ion, *cf.* Dietzell, *Zeitsch. anal. Chem.*, **8**, 153; small quantities of bromine ion in the presence of chlorine ion, Berglung, *Ibid.*, **24**, 184; small quantities of chlorine or bromine ion in the presence of much iodine ion, Bohlig, *Ibid.*, **9**, 315; small quantities of iodine in bromine and bromides, Jorissen, *Ibid.*, **19**, 353; chlorine, bromine, and iodine ion in the presence of each other, Deehan, *Ibid.*, **28**, 705; Jones, *Pharm. Zentralh.*, **25**, 183; Macnair, *Ibid.*, **34**, 519; Hager, *Chem. Zentr.*, 1885, 315; F. Kebler, *Ibid.*, 1893, I., 365; and the collective articles, *Zeitsch. anal. Chem.*, **34**, 599 and 752.

[2] Other methods have been proposed for the detection of the ions of chlorine, bromine, iodine, cyanogen, ferrocyanogen, ferricyanogen, also of chlorate, bromate, and iodate ions (or hydrogen sulphide) in the presence of one another, by Longi, *Zeitsch. anal. Chem.*, **23**, 70; and by Wells and Vulte, *Pharm. Zentralh.*, **31**, 118.

Members of rarer occurrence of the second group.

The anions described in the following Sections 126–129 cannot be given definite positions in the system of analytical grouping. They yield no precipitates with barium chloride, therefore do not belong to the first group; they give precipitates with silver nitrate, and therefore do not belong to the third group; their precipitates with silver nitrate are unstable, decompose with the separation of silver, or are more or less soluble in water or nitric acid, and therefore scarcely belong to the members of more frequent occurrence of the second group.

SEC. 126.

1. Nitrous acid, HNO_2 (Nitrite ion, NO'_2).

1. The anhydride of nitrous acid, nitrogen trioxide, N_2O_3, is, at the ordinary temperature, a brownish-red gas, which, when subjected to cold, can be condensed to a blue liquid. It decomposes in gaseous form to a certain extent into nitric oxide and nitrogen peroxide, $N_2O_3 \rightleftarrows NO+NO_2$. When brought into contact with water, it decomposes (at least the greater portion of it) into nitric oxide gas, which escapes, and nitric acid, which dissolves:

$$3N_2O_3+H_2O=2HNO_3+4NO$$

2. *Nitrous acid*, HNO_2, is not known in the free condition. Although it dissolves in water, it generally decomposes in the process in the above-mentioned manner. The anion NO'_2 combines with metals to form salts, nitrites. These are nearly all soluble in water, and are decomposed on ignition. If treated in the solid condition, or in concentrated solution, with dilute sulphuric acid, nitrous acid is liberated, with the formation of sulphate; the nitrous acid, however, decomposes immediately into nitric oxide (which is oxidised in the air to reddish-brown nitric peroxide) and nitric acid. From very dilute solutions of nitrites, however, it is possible, by means of acidification with acetic acid and distillation, to obtain a liquid in which almost all the nitrous acid is present in aqueous solution in undecomposed form, and since the greater portion will have distilled with the first fractions, it will be present in fairly concentrated condition.

Nitrous acid is a moderately strong acid, about 20 times as strong as acetic acid (dissociation constants $0.45.10^{-3}$). Its salts are slightly hydrolysed in aqueous solution, and in fresh solutions give a faint alkaline reaction. The alkaline reaction is increased if the solutions are allowed to stand, as a portion of the NO'_2 ion is decomposed into NO and NO'_3 and the positive charge disappears, being withdrawn from the $H^·$ ions present in the solution, with the simultaneous formation of hydroxides of the respective cation and the evolution of hydrogen.

Owing to the instability of nitrous acid, it reacts, as do its salts, comparatively easily, effecting both oxidations and reductions; but since the nitrites are nearly all soluble in water, it gives few precipitation reactions. On the other hand, it reacts on many organic substances to form coloured compounds, and especially on aromatic amino compounds, with the formation of diazo and azo compounds.

3. *Silver nitrate* produces in nitrite solutions a white precipitate, soluble in a large quantity of water, especially on heating.

4. *Cobaltous chloride* and *acetic acid* yield with *potassium nitrite*, without further addition (with another nitrite if a *potassium salt* is present), a yellow precipitate of *potassium cobaltinitrite* (*cf.* Sec. 28, 6; Sec. 60, 15).

5. **Ferrous sulphate** in excess produces in neutral nitrite solutions a pale brownish-yellow coloration, which, on the addition of *an acid*, however, is *dark brown*, owing to the nitric oxide dissolving in the ferrous sulphate solution; this coloration is also produced by weaker acids—*acetic acid* or *citric acid*. (Distinction from nitrate ion, which does *not* give the reaction in *acetic acid* or *citric acid* solution.)

6. *Iodine is liberated from iodides, e.g. potassium iodide or zinc iodide*, by means of nitrite solution acidified with sulphuric acid. This sensitive reaction is generally carried out by treating the liquid under examination with a **starch paste of potassium or zinc iodide**[1] and acidifying the liquid with sulphuric acid (Price, Schönbein).

If the solution under examination contains 0·001 per cent. potassium nitrite, the reaction will take place after a few seconds, and if it contains 0·0001 per cent. after a few minutes. The reaction is, of course, only decisive if no other substances which liberate iodine are present, *e.g.* ferric chloride[1] or cupric salts. If the reaction is to be used for the examination of drinking-water, and this disturbing influence is feared, about 300 c.c. may be acidified with acetic acid, distilled, and the first drops received in the zinc iodide starch paste (acidified with sulphuric acid). Naturally no substances which destroy nitrous acid, *e.g.* hydrogen sulphide, must be present in the liquid which is to be distilled.

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[1] A stable zinc iodine starch solution may be obtained as follows: 4 grms. of powdered starch and 20 grms. of zinc chloride are boiled with about 100 grms. of distilled water, the evaporating water being replaced until the crust over the starch is almost completely dissolved; 2 grms. of dry zinc iodide are then added and the whole diluted to 1 litre and filtered. The solution should be kept in well-closed bottles in the dark.

7. *Hydrogen sulphide* produces, immediately in solutions containing free nitrous acid, and gradually in the solutions of neutral alkali nitrites *a white precipitate of sulphur.*

8. On treating water with *indigo solution* until it becomes opaque and then with *hydrochloric acid* and just sufficient *alkali polysulphide* to decolorise the solution completely, and finally adding to the clear filtrate a liquid to be tested for nitrite ion (*e g.* drinking water), *a distinct blue coloration* will appear, even in the case of very considerable dilution (Schönbein). The reaction is only decisive when other oxidising substances are not present.

9. A solution of *diphenylamine* in concentrated sulphuric acid is coloured *deep blue* by nitrites. The reaction is sensitive, but not characteristic, as many other oxidising agents also produce a blue coloration (Sec. 130, 10).

10. *Pyrogallic acid* gives a *brown* coloration to a solution of nitrites acidified with sulphuric acid, even when very dilute (Schonbein).

11. A slightly acid nitrite solution (treated *e.g.* with acetic acid) is not changed by *potassium thiocyanate*, but on the addition of a *strong acid* (nitric acid, hydrochloric acid, sulphuric acid) a dark red coloration will appear; this disappears on the addition of alcohol or on boiling the liquid for a short time. (Distinction from ferric thiocyanate.) When shaken with carbon bisulphide the colouring substance is, to a great extent, taken up by it.

12. *Potassium permanganate* does not react with nitrites in neutral solution. In *acid* solution it is reduced by nitrites and consequently *decolorised.*

13. On treating a liquid containing nitrite ion with a colourless solution of *metaphenylenediamine* in an excess of dilute sulphuric acid[2] or hydrochloric acid, a characteristic *yellow coloration* will appear, even in exceedingly dilute solutions (P. Griess).

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[1] The disturbing influence of ferric salts may be obviated by the addition of disodium hydrogen phosphate (Artmann, *Chem. Zentr.*, 1913, I, 2002).

[2] The solution is decolorised with animal charcoal, and may then be kept for months in a closed vessel.

14. On adding to a liquid containing a nitrite ion a solution of *sulphanilic acid*, mixed with a colourless solution of α-naphthylamine in acetic acid,[1] and heating it at 70° to 80°, a red coloration will appear, turning rapidly to yellow in concentrated solutions, and a permanent pinkish-red coloration in dilute solutions (P. Griess, L. Ilosvay, Lunge, and Lwoff). H. Erdmann (*Zeitsch. angew. Chem.*, **13,** 33) recommends in addition to sulphanilic acid the use of 1·8-*aminonaphthol*-4·6-*disulphonic acid* (so-called *aminonaphthol-K-acid*). This yields a very intense wine-red coloration.[2]

15. For the detection of nitrous acid in concentrated sulphuric acid the following reaction is especially suitable: A trace of *resorcinol* is added to 1 c.c. of the acid, the mixture diluted with 5 c.c. of water and shaken. The smallest trace of nitrous acid may be detected by a yellow coloration (Wilson, Denigès).[3]

16. With regard to the *microchemical detection* of nitrites, see Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 172.

SEC. 127.

2. Hypochlorous acid, HClO (Hypochlorite ion, ClO′).

1. *Hypochlorous acid*, HClO, is not known in the free condition. Its anhydride, *chlorine monoxide*, Cl_2O, is, at the ordinary temperature, a deep yellow gas with an unpleasant irritating odour similar to that of chlorine; it decomposes explosively when heated into chlorine and oxygen, and is soluble in water with the formation of hypochlorous acid. The dilute aqueous solution can be distilled.

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[1] 0·1 grm. of pure (white) α-naphthylamine is dissolved by boiling it for a quarter of an hour with 100 c.c. of water, 5 c.c. of glacial acetic acid, and a solution of 1 grm. of sulphanilic acid in 100 c.c. of water added, and the whole kept in a well-closed vessel, the colour having been removed if necessary by shaking with zinc dust.

[2] With regard to this reaction, see also *Zeitsch. anal. Chem.*, **41,** 703.

[3] Further reagents for the detection of small and very small quantities of nitrous acid are: Diaminobenzoic acid (P. Griess, *Zeitsch. anal. Chem.*, **10,** 92). Carbolic acid and mercurous nitrate (P. C. Plugge, *Ibid.*, **14,** 131; Denigès, *Ibid.*, **36,** 310). Magenta (A. Jorissen, *Ibid.*, **21,** 210). Para-aminobenzene-azodimethylaniline (Meldola, *Ber.*, **17,** 256; *Zeitsch. anal. Chem.*, **24,** 98). Gallic acid (Davy, *Zeitsch. anal. Chem.*, **23,** 72). Antipyrin (Curtman, *Ibid.*, **29,** 194; M. C. Schuyten, *Chem. Zentr.*, 1896, II., 801). Sulphanilic acid and phenol (P. F. Frankland, *Zeitsch. anal. Chem.*, **30,** 713). Potassium ferrocyanide and acetic acid (Scheffer, Deventer, *Ber.*, **26,** 589). Concentrated sulphuric acid and cuprous oxide (Sabatier, *Chem. Zentr.*, 1896, II., 318). Aniline and glacial acetic acid (Denigès, *Zeitsch. anal. Chem.*, **36,** 310). Naphthionic acid (Riegler, *Ibid.*, **35,** 677; **36,** 306). Pyrogalloldimethylester (Meyerfeld, *Chem. Zeit.*, **34,** 948). Benzidine, *o*-toluidine or dianisidine (Primot, *Chem. Zentr.*, 1912, II., 1846). Diphenylbenzidine (Letts and Rea, *Ibid.*, 1914, II., 263). Indol (Dané, *Ibid.*, 1910, II., 1405; 1911, I., 1763).

Hypochlorous acid is a very weak acid with the dissociation constants $3.7.10^{\;2}$ at 17°.

2. The hypochlorous acid *salts*, the *hypochlorites*, occur as a rule with chlorides, for example, in chloride of lime solution, eau de Javelle, etc. (Their formation is based on the hydrolytic decomposition of chlorine by water: $Cl_2+H_2O \rightleftarrows H^{\cdot}+Cl'+HClO$, for example, $Cl_2+2NaOH=NaClO+NaCl+H_2O$.) Their solutions undergo partial hydrolytic dissociation corresponding to the low strength of the hypochlorous acid; they change when boiled. Chlorine and chlorate ions are formed from the hypochlorite ion (in dilute solutions without the evolution of oxygen, in concentrated solutions, or in the presence of suitable catalysts with such evolution). On mixing a solution of chloride of lime with an excess of hydrochloric or sulphuric acid, chlorine is evolved, whereas on the introduction of carbon dioxide into chloride of lime solution, hypochlorous acid or chlorine monoxide is liberated.

3. *Silver nitrate* precipitates silver chloride from chloride of lime solution which has been so neutralised with nitric acid that it no longer has the odour of chlorine; the silver hypochlorite temporarily formed very soon decomposes into silver chloride and silver chlorate ($3AgClO=AgClO_3+2AgCl$).

4. *Lead nitrate* or *lead acetate* produces a precipitate which is at first white, gradually turns orange-red, and finally, owing to the formation of peroxide, becomes brown.[1]

5. *Manganous salts* yield brownish-black precipitates of hydrated manganese dioxide.

6. *Free hypochlorous acid* produces, when acting on *mercury*, yellowish-brown mercuric oxychloride (whereas chlorine yields mercurous chloride). If there is so little hypochlorous acid present with much chlorine that, after shaking, the colour of the precipitate does not clearly indicate hypochlorous acid, the precipitate which is formed after long shaking should be treated with hydrochloric acid (which dissolves the oxychloride, but leaves the mercurous chloride unchanged), and then filtered off; hypochlorous acid will be recognised by the presence of mercuric chloride in the filtrate. *Hypochlorites* may be detected more readily than the free acid by

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[1] R. Fresonius has based on this reaction a method of separating hypochlorite ion from chlorate ion, *i.e.* of detecting chlorate in chloride of lime (*Zeitsch. anal. Chem.*, **34**, 434). The chloride of lime solution is treated with lead acetate, the liquid filtered, the excess of lead in the filtrate removed by sulphuric acid, and the test for chlorate ion made with indigo solution and sulphur dioxide (Sec. 131, 5).

shaking their solutions with mercury, because in their presence yellow mercuric oxide (which gradually turns red) is formed, and this adheres to the sides of the glass tube when shaken. Chlorites and chlorates have no action upon mercury (Wolters).

7. On shaking a solution of free hypochlorous acid with *powdered silver* oxygen escapes. (Distinction from chlorine.)

8. A solution of *potassium permanganate* is not decolorised. *Litmus* and *indigo tincture* are slightly decolorised, even by alkaline solutions, and considerably on the addition of an acid.

9. If a solution of *arsenious acid* in hydrochloric acid is rendered blue by means of *indigo solution*, and a solution of chloride of lime added with continuous stirring, the colour will only begin to disappear when all the arsenious acid has been converted into arsenic acid.

SEC. 128.

3. Hypophosphorous acid, HPH_2O_2 (Hypophosphite ion, $PH_2O'_2$).

1. The concentrated solution is of the consistency of syrup, and resembles that of phosphorous acid (Sec. 113), to which it is similar in that, when heated in the absence of air, it is decomposed into phosphoric acid and hydrogen phosphide gas, which does not ignite spontaneously. Hypophosphorous acid is a moderately strong monobasic acid.

2. Nearly all the *salts* of hypophosphorous acid, the *hypophosphites*, are readily soluble in water; they are all decomposed on ignition into phosphates and, as a rule, into hydrogen phosphide, gas which ignites spontaneously, and portions of which are decomposed into phosphorus and hydrogen.

3. *Barium chloride*, *calcium chloride*, and *lead acetate* do not give precipitates. (Distinction from phosphites).

4. *Silver nitrate* produces with hypophosphites at first a white precipitate of silver hypophosphite, which turns black even at the ordinary temperature, and more rapidly when heated, with the separation of metallic silver.

5. Hypophosphites precipitate mercurous chloride from a solution containing an excess of *mercuric chloride*, slowly in the cold, and more rapidly when heated.

6. On treating a nitric acid solution of *ammonium molybdate* (Sec, 25, C, 4, p. 111) with a liquid containing a hypophosphite ion, and adding a few drops of an aqueous *sulphur dioxide solution*, a

blue precipitate, or a fine dark-blue coloration, will be formed on gentle heating. Hydrogen sulphide, thiosulphates, chlorates, and stannous chloride prevent this very sensitive reaction (Millard).

7. A solution of *cupric sulphate* produces with hypophosphorous acid and with its salts, on heating, a reddish-brown precipitate of copper hydride (cuprous hydride), Cu_2H_2.

8. When brought into contact with *zinc* and dilute *sulphuric acid* hypophosphorous acid yields hydrogen containing hydrogen phosphide (*cf.* Phosphorous acid, Sec. 113, 11).

SEC. 129.

4. Hydronitric acid, HN_3 (Azide ion, N'_3).

1. *Hydronitric acid*[1] is a clear, colourless, mobile liquid with a very strong odour, reminiscent of hydrogen phosphide. Its vapours have a pronounced action upon the mucous membrane, and explode violently when brought into contact with a flame. Its aqueous solution is colourless, has an acid reaction, and is dissociated only to a moderate degree (to about the same extent as acetic acid, dissociation constants $1.9 . 10^{-5}$ at 25°). It dissolves metals to azides with the evolution of hydrogen. By this means, as by *reducing agents* generally, it is reduced to ammonia and hydrazine: $HN_3+3H_2=NH_3+N_2H_4$. *Oxidising agents*, especially *iodine*, decompose it with the evolution of nitrogen: $2N_3H+I_2=3N_2+2HI$. The latter reaction is considerably accelerated by the addition of a little sodium thiosulphate. Ceric salts are also very suitable for the decomposition of hydronitric acid or of the azides; they are reduced thereby to cerous salts, whilst nitrogen escapes. Fuming *hydriodic acid* causes the formation of nitrogen, ammonia, and iodine: $HN_3+2HI=N_2+NH_3+I_2$ (K. A. Hofmann and others, Hock).

2. The *salts* of hydronitric acid, the *azides*, also called *nitrides*, decompose readily, and explode violently on heating or receiving a shock or blow, being decomposed into the elements. Most metal azides are soluble in water.

3. *Silver nitrate* produces *a white caseous precipitate of silver azide*, AgN_3 (similar in appearance to silver chloride), which is, however, soluble in nitric acid.

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[1] Hydronitric acid, as also its salts, are more or less strongly explosive substances, which are decomposed very readily on heating, with the utmost violence. The greatest care, therefore, must be taken when dealing with them.

4. *Mercuric nitrate* and *lead nitrate* or *lead acetate* also produce precipitates of the respective azides.

5. On treating hydronitric acid or the solution of an azide with *ferric chloride solution* in excess, a characteristic deep red coloration of the solution will appear (L. M. Dennis and A. W. Browne, *Zeitsch. anorgan. Chem.*, **40**, 99).

THIRD GROUP OF INORGANIC ACIDS.

Anions, which are precipitated neither by Barium Salts nor by Silver Salts.

Nitric acid, chloric acid —or nitrate ion, chlorate ion—(perchloric acid or perchlorate ion).

SEC. 130.

(a) Nitric acid, HNO_3 (Nitrate ion, NO'_3).

1. *Nitrogen pentoxide* (the anhydride of nitric acid), N_2O_5, crystallises in hexagonal prisms. It melts at 29·5°, and boils at 45° (Deville), but at this temperature decomposes perceptibly with the evolution of brown nitrogen peroxide vapours. Absolute *nitric acid* (never quite anhydrous) is a colourless (red, if it contains hyponitrous acid) liquid of sp. gr. 1·52, which is very corrosive, has a strong oxidising action, rapidly destroys organic substances, and colours many substances containing nitrogen a bright yellow; it fumes in the air and boils at 86°. Nitric acid belongs to the strongest of the known acids, and is extensively dissociated in aqueous solution.

2. The neutral *salts* of nitric acid, the *nitrates*, are, with few exceptions (cinchonamine, Arnaud and Padé; nitron, H. Busch), soluble in water; on the other hand, a few of the basic nitric acid salts are insoluble in water. All nitrates are decomposed when strongly ignited. In this process the nitrates of the alkali metals are converted first into nitrites, with the evolution of oxygen, and then into oxides, while oxygen and nitrogen escape; other nitrates yield oxygen and *nitrogen peroxide;* many (hydrated) allow nitric acid to escape. This behaviour may be especially well observed if the heating is carried out in a **small ignition tube** (p. 55, or Sec. 152, Rubric number 2). Escaping oxygen may be recognised by the fact that it causes a glowing splinter of wood, introduced into it, to ignite.

3. If a nitrate is thrown on to **glowing charcoal,** or if *charcoal*

or an organic substance, *e.g. paper*, is brought into contact with a **melting nitrate,** an *explosive fusion* takes place, that is to say, the charcoal burns at the expense of the oxygen of the nitrate, emitting bright sparks.

4. On mixing a nitrate with powdered *potassium cyanide* and heating the mixture on platinum foil, there is vigorous explosive fusion, accompanied by a distinct incandescence and a report. *This test must only be carried out on a very small scale.*

5. On mixing a nitrate with **copper filings** and heating the mixture in a test-tube with concentrated sulphuric acid, the air in the tube will become *brownish-red,* while the *nitric oxide* liberated in the oxidation of the copper by nitric acid combines with the atmospheric oxygen to form nitrogen peroxide. The coloration is most distinctly visible on looking lengthways through the tube.

6. On treating the solution of a nitrate with an equal volume of concentrated **sulphuric acid,** free from nitric and nitrous acids, allowing it to cool, and then pouring a concentrated solution of **ferrous sulphate** over it, in such a way that the liquids do not mix, *the zone at the point of contact will first become purple and later brown,* or reddish in the case of very small quantities of nitrate ion. On mixing the liquid slightly the brown zone is extended. The nitric acid oxidises a portion of the ferrous ion to ferric ion, and is thereby reduced to nitric oxide, which dissolves in the solution of the excess of ferrous salt, giving a brownish-black colour : $2HNO_3 + (6+x)FeSO_4 + 3H_2SO_4 = 3Fe_2(SO_4)_3 + [2NO + xFeSO_4] + 4H_2O$. Large quantities of chlorides influence the sensitiveness of the reaction.[1] A similar reaction takes place in the presence of selenious acid, but on mixing the liquid and allowing it to stand red selenium separates (Wittstock).

7. On boiling a little hydrochloric acid in a test-tube, adding one or two drops of a very dilute **solution of indigo in sulphuric acid** and boiling it again, the liquid will remain blue, provided the hydrochloric acid contains no free chlorine. On now adding a nitrate in solid form or in solution to the pale blue solution and again heating it to boiling point, *the liquid will lose its colour, owing to the destruction of the indigotin.* The addition of sodium chloride increases the sensitiveness of what is already a very sensitive reaction. It should, however, be noted that other oxidising agents, especially free chlorine, also cause decolorisation.

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[1] In this connection; see also W. Manchot and Huttner, *Liebig's Ann.*, **372**, 153 ; *Chem. Zentr.*, 1910, I., 1685 ; Bellucci, *Chem. Zentr.*, 1917, II., 426.

8. On dissolving a little **brucine** in pure *concentrated sulphuric acid* [1] in a porcelain dish or on a clock glass, and applying to the edge of the fluid a drop of a liquid containing nitrate ion, the solution will at once assume a fine red colour at the point of contact. This reaction is exceedingly sensitive. The bright red soon changes to yellowish-red. Chlorate ion gives a similar coloration, as does nitrite ion under certain conditions.[2]

9. On dissolving 1 part of *phenol* (carbolic acid) in 4 parts of concentrated *sulphuric acid*, adding 2 parts of water, and treating one or two drops of this liquid with a solid nitrate (or the residue left on evaporating a small quantity of spring water containing a nitrate), a *reddish-brown coloration* will appear, owing to the formation of a nitro compound of the phenol. This coloration, which, on the addition of one or two drops of concentrated ammonia solutions, sometimes turns transitorily green, eventually becomes yellow, owing to the formation of ammonium nitrophenol. This is a very sensitive reaction (H. Sprengel).

The reaction may also be carried out either by adding to pure *concentrated sulphuric acid* one or two drops of the liquid being tested for nitrate ion, and then a crystal of phenol, and heating it; or also by rendering the liquid under examination strongly acid with *hydrochloric acid*, adding a little phenol, and heating it to about 80° to 90°. *In the presence of nitrate ion there will always appear a dark coloration*, which, as a rule, is *red* or *brown*, and under certain conditions may be *green* (H. Hager).

10. On pouring a little pure concentrated sulphuric acid on to a few crystals of diphenylamine, adding a little water, and mixing the resulting solution with more concentrated sulphuric acid, an excellent

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[1] The ordinary pure commercial sulphuric acid generally gives with brucine a pinkish-red coloration of its own accord, owing to its containing a small quantity of the oxygen compounds of nitrogen. On diluting such an acid with water to a sp. gr. of 1·4 and boiling it (preferably in a platinum dish) it may be freed from such impurities.

[2] *Cf.* L. W. Winkler, *Zeitsch. angew. Chem.*, **15**, 170, according to whom, on mixing the solution under examination with $\frac{1}{2}$ its volume of concentrated sulphuric acid, and, after cooling, adding a little brucine, nitrite ion gives first a cherry-red, then orange, and finally a yellow coloration. Nitrate ion only reacts under these conditions if it is present in considerable quantity, but on adding the solution under examination drop by drop to 3 or 4 volumes of concentrated sulphuric acid and dissolving a little brucine in the cooled solution, only nitrate ion reacts. On mixing the liquid with 2 volumes of concentrated sulphuric acid and dissolving a little brucine in the still hot liquid, nitrite and nitrate ions will react, producing a lemon-yellow colour. *Cf.* also G. Lunge, *Zeitsch. angew. Chem.*, **15**, 241; as also Soltsien, *Chem. Zentr.*, 1906, II., 1020.

reagent for nitric acid is obtained, which is most suitable for the detection of small quantities if it contains only 1 mgrm. of diphenylamine in 10 c.c. If about 0·5 c.c. of this solution is placed on a clock glass or the reversed lid of a porcelain crucible, and a drop of the liquid being tested for nitrate ion allowed to fall in the middle of the reagent, a fine blue-coloured ring will be formed, the extent of which depends upon the degree in which the liquids mix (E. Kopp).

This very sensitive reaction may also be carried out by mixing a few drops of a solution of diphenylamine sulphate with the solution being tested for nitrate ion, and then adding pure concentrated sulphuric acid so that two layers are formed. The blue coloration gradually turns to green, and finally disappears altogether.[1] The addition of chlorine ion increases the sensitiveness of the reaction. The interpretation of the reaction requires care, as many other oxidising substances, *e.g.* nitrites, chlorates, hypochlorites, bromates, iodates, vanadates, chromates, permanganates, and molybdates, and also ferric salts, hydrogen peroxide, barium peroxide, etc., yield blue colorations (Laar). The solutions of *diphenyl-o-toluidine* gives a similar and more sensitive reaction. It is, however, also produced by nitrites, chlorates, etc. (Häussermann and Bauer, *Ber.*, **31**, 2987). *Diphenylbenzidine* reacts in the same manner (Letts and Rea, *Chem. Zentr.*, 1914, II., 263).

11. On adding to a solution of a nitrate a few drops of a solution of *paratoluidine sulphate*, and then, carefully, an equal volume of concentrated *sulphuric acid*, so that the liquids do not mix, there will immediately appear at the point of contact of the two liquids a *red zone*, the colour of which gradually changes to dark yellow.[2] The reaction is not so sensitive as those with brucine or diphenylamine, but, on the other hand, it is suitable for detecting nitrate ion in the presence of smaller quantities of nitrite ion, as the latter gives at first a yellowish or yellowish-brown coloration, which only after some time is converted into red (Longi).

Chlorates and other oxidising agents produce similar colorations.

12. On heating a solid nitrate with a small quantity of a solution

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[1] With regard to this reaction, *cf. inter alios* Cimmino, *Zeitsch. anal. Chem.*, **38**, 429; Tillmans and Sutthof, *Ibid.*, **50**, 473; Rickow, *Chem. Zentr.*, 1905, I., 402; Pinerua Alvarez, *Ibid.*, 1905, I., 1431; Frerichs, *Ibid.*, 1905, I., 957; Soltsien, *Ibid.*, 1906, II., 1020; Withers and Ray, *Ibid.*, 1911, II., 489; de Jong, *Ibid.*, 1913, II., 1824.

[2] The reaction may also be produced with a sulphuric acid solution of an aniline oil containing aniline and paratoluidine. C. D. Braun recommended such a reaction as far back as 1867 (*Zeitsch. anal. Chem.*, **6**, 72). His method of carrying out the reaction differs slightly from that of Longi.

of *salicylic acid* in *concentrated sulphuric acid* (2 grms. to 30 c.c.); or on evaporating a nitrate solution with the reagent, heating it until sulphuric acid vapours escape, and rendering the residue alkaline with alkali hydroxide, a yellow or orange coloration will appear The reaction may also be used for the detection of nitrates in the presence of organic substances. In this case the substance under examination is heated with the reagent until sulphur dioxide vapours escape, the carbonised mass extracted with water, the solution evaporated, and alkali hydroxide added. The reaction depends on the formation of nitrosalicylic acid (Tingle, *Chem. Zentr.*, 1915, II. 202; 1916, I., 1041).

13. On treating the solution of a *manganous salt* in *fuming hydrochloric acid* with a few drops of a solution containing nitrate ion, a dark greenish-black coloration with a yellow tinge will appear owing to the formation of $MnCl_4$. The reaction is also produced by chlorates, hypochlorites, chromates, and lead peroxide (L. L. de Koninck, *Chem. Zentr.*, 1902, II., 14).

14. Very small quantities of nitrate ion may also be detected by reducing them first to nitrite ion. This may be done by the we or dry method; the wet method consists in stirring the solution o nitric acid for a short time with a zinc rod, or heating that of th nitrate with finely divided *zinc*, preferably with *zinc amalgam*, and then filtering it (Schönbein); the dry method consists in fusing the substance under examination with pure sodium carbonate at moderate heat, extracting the cooled mass with water, and filtering th solution. If one of these filtrates is brought into contact with potassium iodide starch paste and dilute pure sulphuric acid, th liquid will be rendered blue by the starch iodide (*cf.* Sec. 119, 10 as also Soltsein, *Chem. Zentr.*, 1906, II., 1020).[1]

15. On adding a small quantity of a 10 per cent. solution o nitron[2] in acetic acid to a solution of a nitrate slightly acidified with sulphuric acid, *a white precipitate of nitron nitrate is immediately produced.* If the nitrate solution is very dilute, crystalline separation takes place only on standing. The reaction is, however, no characteristic of nitrate ion, as other anions give nitron compound

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[1] With regard to further reactions for the detection of small quantities o nitrate, *cf.* Breal, *Chem. Zentr.*, 1888, 864; Lindo, *Ibid.*, 1888, 1442; Rosenfeld *Zeitsch. anal. Chem.*, **29**, 661; E. Luther and v. Udranszky, *Ibid.*, **29**, 732 Vitali and Bringhelli, *Ibid.*, **38**, 540; Denigès, *Chem. Zentr.*, 1911, II, 239 Iwanow, *Ibid.*, 1913, I., 844.

[2] Nitron (synthetically prepared by Busch) is the base diphenylenedianilo dihydrotriazole. It may be procured from E. Merck in Darmstadt.

which dissolve with difficulty, such as bromide, iodide, nitrite, bromate, chlorate, perchlorate, thiocyanate, ferro- and ferricyanogen, and picrate ions. Nitron oxalate dissolves also with difficulty in water, but, on the other hand, it does not separate in strong acid solution (M. Busch, *Ber.*, **38**, 861).

16. On treating a strong *alkali hydroxide solution* with a nitrate, and adding a little *aluminium* or a little *zinc and iron filings*, ammonia will be evolved on gentle heating, and may be easily recognised by the methods described in Sec. 30, 4, 10, or 12. Nitrite ion, of course, gives the same reaction.

17. With regard to the *microchemical detection* of nitric acid salts, see Haushofer, *Mikroskopische Reaktionen*, p. 115; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 170; Ellram, *Chem. Zentr.*, 1896, II., 99; Brauns, *Ibid.*, 1897, I., 434; Schröder van der Kolk, *Ibid.*, 1897, I., 1173; Emich v. Donau, *Ibid.*, 1907, II., 1444.

SEC. 131.

(b) Chloric acid, $HClO_3$ (Chlorate ion, ClO'_3).

1. *Chloric acid* is only known in aqueous solution; its most concentrated solution is a thick colourless or pale yellow liquid with a faint odour similar to that of nitric acid, and a strongly acid taste. It reddens litmus and then bleaches it. In the dilute condition it has neither colour nor odour. Chloric acid has a strong oxidising action; it is a very strong acid, and even in 0·5 *N*-solutions is dissociated to the extent of 88 per cent.

2. The chloric acid *salts*, *chlorates*, are all soluble in water. They are decomposed on ignition, either into gaseous oxygen, which escapes, and chloride, or there remains a residue of oxide, whilst oxygen and chlorine escape (chlorates of the earth metals). This decomposition may be easily observed if the salts are **heated in a small** ignition tube (p. 55, and Sec. 150, rubric number 3), by means of which the escaping gas may be recognised as oxygen on the introduction of a *glowing match*.

3. Chlorates, when heated with **charcoal** or with an **organic substance,** *fuse explosively*, more violently than do the nitrates.

4. If a chlorate is mixed with *potassium cyanide* and the mixture heated on platinum foil, *explosive fusion* will take place, combined with a loud report and incandescence, even in the case of very small quantities. *The test should only be made with minute quantities.*

5. On colouring the solution of a chlorate light blue with a small

quantity of a **solution of indigo in sulphuric acid,** adding a lit dilute *sulphuric acid*, and then, drop by drop, and carefully, a sm quantity of aqueous *sulphur dioxide* or *sodium sulphite solut the colour of the indigo will immediately disappear.* The cause this reaction, as sensitive as it is characteristic, is that the sulpl dioxide reduces the chlorate ion to chlorine or to the lower oxyg compounds of chlorine, which then decolorise the indigo. An exc of sulphite ion must, of course, be avoided, as otherwise sulph ion and chlorine ion will be formed.

6. Solutions containing chlorate ion are slowly decomposed l the action of **hydrochloric acid,** more rapidly at a higher temper ture (70°), whilst water, *chlorine*, and *chlorine dioxide*, ClO_2, a formed.[1] The test-tube in which the experiment is made w *become filled with greenish-yellow gas with a very unpleasant odo similar to that of chlorine; the hydrochloric acid will be colour greenish-yellow.* If the hydrochloric acid was rendered blue l indigo solution, the indigo blue will be destroyed at once, even the presence of a very small quantity of a chlorate.

7. If a few drops of **concentrated sulphuric acid** are plac on a clock glass and a little chlorate added, chloric acid is fir liberated; this, however, decomposes immediately into *perchlor acid, chlorine dioxide*, and water :

$$3HClO_3=2ClO_2+HClO_4+H_2O$$

The chlorine dioxide colours the sulphuric acid bright yellow, an apart from this, may be recognised by its *characteristic and ve unpleasant odour. Heat must be avoided in this experiment and sm quantities used,* as otherwise the decomposition takes place wit such violence that an explosion occurs, *since greenish-yellow chlori dioxide explodes even at 60°.*

8. If a drop of a solution of *aniline sulphate* is added to tl solution of a chlorate in concentrated sulphuric acid (prepar according to 7), the liquid will assume a *deep blue coloration*, whi may be intensified by the addition of a few drops of *water*. This is very sensitive reaction, and is not given by nitrate ion (Vitali).

A solution of *aniline hydrochloride* in strong hydrochloric ac produces with chlorates in the solid form, or in solution, a viol coloration, which soon becomes blue. This is a very sensitiv reaction (Virgili, *Chem. Zentr.*, 1909, I., 1503). Pieraerts (*Che*

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[1] With regard to the course of the reaction, *cf.* Sand. *Zeitsch. physik. Chem* **50**, 465 ; and Luther and MacDougall, *Ibid.*, **55**, 477 ; and **62**, 199.

Zentr., 1913, I., 1063) recommends the use of an alcoholic solution of aniline. The colouring matter may be extracted by shaking with ether or amyl alcohol. Pozzi Escot (*Chem. Zentr.*, 1913, II., 173) recommends as being more sensitive the otherwise analogous colour reaction with benzidine and sulphuric acid.

9. Chlorate ion behaves like nitrate ion towards solutions of *brucine, diphenylamine, paratoluidine*, and *phenol in concentrated sulphuric acid*, or at least in such a similar manner that it is not possible to distinguish with certainty between them by means of these reagents. On the other hand, chlorate ion may be distinguished from nitrate ion by the test given in 8, as also by means of phenol in hydrochloric acid solution (*cf.* Sec. 130, 9), since chlorate ion produces, according to the conditions, an orange-red turbidity or a transitory yellow coloration in such a solution.

10. On *boiling* a dilute aqueous solution of an alkali chlorate with Gladstone and Tribe's *copper zinc element*,[1] *complete reduction to alkali chloride* will take place, with the separation of zinc oxide (Thorpe and Eccles). Chlorate ion in a solution acidified with sulphuric acid is converted into chlorine ion by the nascent hydrogen which is liberated on the addition of zinc. Chlorates are also reduced to chlorides in dilute sulphuric acid solution by means of finely divided *aluminium*. (Distinction from perchlorates. Venditori, *Chem. Zentr*, 1908, I., 4.) Chlorates (but not as a rule perchlorates) are also reduced by other reducing agents, *hydrogen sulphide, ammonium sulphide, hydrazine sulphate, ferrous ammonium sulphate, sulphur dioxide, nitrous acid, iron with dilute sulphuric acid, formic acid* (Vitali, *Chem. Zentr.*, 1910, I., 1105).

SEC. 132.

Summary and Remarks on Anions, Group III.

1. Of the reactions described for the detection of *nitrate ion*, those with ferrous sulphate and sulphuric acid, those with copper filings and sulphuric acid, and also those which depend on the formation of nitrite ion or ammonia, give the most trustworthy results, since explosion with charcoal, detonation with potassium cyanide, decoloration of the indigo solution, and the sensitive reactions with brucine, diphenylamine, and paratoluidine do not afford a definite

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[1] The copper zinc element is prepared by treating thin zinc foil with a 1 per cent. cupric sulphate solution, whereby the zinc becomes black owing to the deposited copper. When washed and dried the element is ready for use.

distinction from chlorate ion. They are, therefore, only of val when there is no chlorate ion and no other disturbing substan present. The reaction with nitron (15) is also not absolut decisive. *Free nitric acid* may be recognised in a liquid by evapor ing it to dryness in a porcelain dish on the water-bath, after havi thrown in a few shavings of quill. A yellow coloration of th shavings indicates the presence of nitric acid (Runge).

2. The presence or absence of *chlorate ion* is indicated wi the greatest certainty, when other oxygen compounds of chlorine a not present, by igniting the substance with sodium carbona dissolving the mass in water, and then testing the solution wi silver nitrate. If a chlorate was present it will have been convert on ignition into chloride, and a precipitate of silver chloride w then be obtained. This test, however, is so simple only when chloride is simultaneously present. In the presence of chlorid silver nitrate must be added so long as a precipitate forms, a only when this has been filtered off should the liquid be evaporate with the addition of pure sodium carbonate, and the residue ignite As a rule, however, it is not necessary to adopt this complicat course, as the reactions with concentrated sulphuric acid, wi indigo and sulphurous acid, as also with aniline sulphate, indica the presence of chlorate ion with the greatest certainty, even wh nitrates are present.[1]

3. If *nitrate ion* is to be detected *in the presence of a large quanti of chlorate ion*, the substance should be treated with sodium carbona in excess, evaporated, and, if necessary, the residue ignited gent but for a sufficient time, to convert the chlorate into chloride, an this residue then tested for nitrate or nitrite ion.

4. If *nitrate ion* is to be detected in the presence of *nitrite io* pure urea is introduced into the aqueous solution, and the liqu added little by little to a solution of urea in dilute sulphuric aci The nitrite ion will immediately be decomposed, with the evolutio of nitrogen and carbon dioxide. If, when the decomposition complete (*i.e.* after about 24 hours), potassium iodide and thi starch paste are added, the liquid remains colourless. On no adding a little finely divided zinc, the resulting blue coloratio (Sec. 130, 14) will indicate the presence of nitrate ion (Piccini).

According to Fischer and Steinbach (*Zeitsch. anorgan. Chem* **78**, 134; *Chem. Zentr.*, 1913, I., 61) nitrites may also be remove by adding methyl alcohol, drop by drop, to the solution acidified with sulphuric acid and simultaneously introducing a strong current of air or carbon dioxide. The methyl ester of nitrous acid is almost immediately formed, and is carried off with the current of gas. Sommer and Pincus (*Ber.*, **48**, 1963) recommend the addition of hydronitric acid or sodium azide and sulphuric acid; the nitrous acid is then decomposed in accordance with the formula:

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[1] With regard to the detection of chlorate ion in the presence of nitrate ion *cf.* **Béhal**, *Chem. Zentr.*, 1886, 124.

$$HN_3+HNO_2=N_2+N_2O+H_2O$$

Sen and Day (*Zeitsch. anorgan. Chem.*, **71**, 236, and **74**, 51; *Chem. Zentr.*, 1911, II., 789; 1912, I., 1250) recommend the addition of hydrazine sulphate to the nitrite solution. The nitrous acid is thereby decomposed in accordance with the equations:

$$N_2H_4+2HNO_2=3H_2O+N_2+N_2O$$
$$\text{and}\quad N_2H_4+HNO_2=NH_3+N_2O+H_2O$$

The anions dealt with in the last sections may be amplified by a series of others not described in detail in this book, such as those of the bromates, perbromates, periodates, the manganates, and permanganates; further, the reactions of the hypoiodite and hypobromite ions corresponding to the hypochlorites are not specially described. In these and similar cases the general behaviour will, on the one hand, indicate the oxidation stage to which the anion corresponds, and, on the other hand, the metalloid or metal contained in it may, after reduction, be easily recognised. In specific cases reference must be made to the literature on the subject. The anions in question are, however, on the one hand, of rarer occurrence and less important, or, on the other hand, like permanganate ion, have such characteristic properties (violet colour) that they cannot easily be overlooked, especially as attention is drawn to them in the analytical course. With regard to a few suggestions for detecting several of the anions in question in the presence of one another, and of other anions, reference should be made to Longi, *Zeitsch. anal. Chem.*, **23**, 70, 149, 352; Alvarez and Jean, *Chem. Zentr.*, 1896, II., 514; A. Monnier, *Ibid.*, 1917, I., 691. With regard to the detection of perchlorate ion in the presence of chlorine ion, chlorate ion, etc., *cf.* also Gooch and Kreider, *Zeitsch. anal. Chem.*, **35**, 85; with regard to the detection of chlorate ion in the presence of hypochlorite ion, *cf.* Wischo, *Chem. Zentr.*, 1917, II., 133.

SEC. 133.

Perchloric acid, $HClO_4$ (Perchlorate ion, ClO'_4).

1. *Perchloric acid* is a colourless, corrosive liquid, which fumes strongly in the air, and, after being kept for some time, decomposes rapidly and with a violent explosion when dropped on to charcoal, wood, or paper. It forms needle-shaped crystals containing one molecule of water, $HClO_4 + H_2O$. When strongly heated it dissolves in water, and behaves then like a strong acid. The dilute solution on being distilled yields first water, then dilute, and finally concentrated acid.

2. All the *perchloric acid salts, perchlorates,* are soluble in water; the greater number dissolve easily, all are decomposed on ignition, those of the alkali metals leaving a residue of chlorides, while oxygen is evolved.

3. *Potassium salts* produce in not too dilute solutions a *white, crystalline precipitate of potassium perchlorate,* $KClO_4$, which dissolves with difficulty in water and not at all in alcohol.

4. *Barium and silver salts* are not precipitated.

5. *Concentrated sulphuric acid* does *not* decompose perchloric acid in the cold, and only with difficulty when heated. (Distinction from chloric acid.)

6. *Hydrochloric acid, nitric acid,* and *sulphur dioxide* do not decompose an aqueous solution of perchloric acid or perchlorates, and indigo solution, previously added, is therefore not decolorised. (Distinction from all other acids of chlorine.)

7. Alkali perchlorates are not reduced by a *copper-zinc element* (Sec. 131, 10). (Distinction from chlorates.) Speaking generally, the perchlorates show great resistance to reducing agents, and only the compounds of *trivalent titanium, hydrosulphurous acid* ($H_2S_2O_4$), and the *lower oxidation stages of vanadium and molybdenum* (also *tungsten*) reduce perchlorates to chlorides (Rothmund, *Zeitsch. anorgan. Chem.*, **62**, 108; *Chem. Zentr.*, 1909, I., 1831).

8. On fusing perchlorates with chlorides, *e.g. zinc chloride, chlorine* is liberated. *If the reaction takes place in a current of carbon dioxide, and the gas is conducted through potassium iodide solution, iodine is liberated.* If nitrates are present, they may be removed by heating them with very strong hydrochloric acid, evaporating them to dryness with manganous chloride and concentrated hydrochloric acid, and again heating them with hydrochloric acid. After the manganese has been precipitated with sodium carbonate, the mixture is evaporated to dryness, and the residue fused with melted zinc chloride (Gooch and Kreider, *Zeitsch. anorgan. Chem.*, 7, 13; *Chem. Zentr.*, 1894, II., 343 and 494).

9. With regard to the *microchemical detection* of perchlorate, especially in Chili nitre, *cf.* Sjollema, *Zeitsch. anal. Chem.*, **37**, 44; H. Fresenius and Bayerlein, *Ibid.*, **37**, 501; Breukeleveen, *Chem. Zentr.*, 1898, I., 960; Behrens-Kley, *Mikrochemische Analyse*, 3rd ed., p. 173.

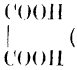
B. ORGANIC ACIDS.

FIRST GROUP.

The normal calcium salts of the first group are practically insoluble, or dissolve with difficulty, in water or in alcohol of at least 70 per cent : *Oxalic acid, tartaric acid (racemic acid), citric acid, malic acid, succinic acid, cinnamic acid.*

FIRST DIVISION

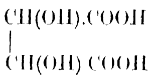
The acids of the first division decompose wholly or partially when heated.[1] They are oxidised when boiled with nitric acid.[2] They dissolve with difficulty in ether (oxalic acid not to the same extent as the others). The solutions of their normal alkali salts are not precipitated by ferric chloride solution prepared in the cold (Sec. 138, 5), but when mixed in definite proportions give at most an opalescent turbidity : *Oxalic acid, tartaric acid (racemic acid), citric acid, malic acid.*

(a) Oxalic acid  (Oxalate ion, $C_2O''_4$).

$$\begin{array}{l}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{array}$$

Its reactions have been described in Sec. 110.

Sec. 134.

(b) **Tartaric acid**  (Tartrate ion, $C_4H_4O''_6$).

$$\begin{array}{l}\mathrm{CH(OH).COOH}\\ |\\ \mathrm{CH(OH).COOH}\end{array}$$

1. *Tartaric acid* is known in several stereoisomeric forms, that is to say, forms of the same constitution but having a different spatial arrangement of the atoms within the molecule. One is termed *d*-tartaric acid or dextro-rotatory tartaric acid, and the other *l*-tartaric acid or lævo-rotatory tartaric acid. Both are the so-called mirror isomers ; they are distinguished from one another, as are their salts, only by the form of their crystals (state of opposed semihedra) [3] and by the direction of their optical

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[1] Oxalic acid, carefully heated, sublimes partly undecomposed.

[2] The decomposition of oxalic acid by boiling nitric acid into carbon dioxide and water only takes place slowly.

[3] Semihedral crystals show a less symmetrical arrangement of the atoms, so that in certain forms of crystals only half of the surfaces occur which are essential to the complete symmetry of the crystalline system in question. Opposed semihedral forms behave towards each other like an object and its mirrored reflection, but cannot be made to coincide by turning them round (Enantiomorphism).

activity;[1] the former in aqueous solution diverts the plane of the polarised beam of light to the right, the latter to the left. The specific power of rotation[2] is very considerably increased by the simultaneous presence of molybdate, tungstate, uranyl, and beryllium ions in the solution. The two isomeric tartaric acids do not differ in their chemical reactions. When equimolecular proportions of the two acids come into contact with one another, a third acid is formed, *i.e.* the ($d+l$)-tartaric acid, also termed *racemic acid* (Sec. 135). It is optically inactive. A fourth variety, also optically inactive, is the *i*-tartaric acid, also termed *mesotartaric acid* or *antitartaric acid*. The inactivity of this is due to an intromolecular equilibrium.

2. Ordinary tartaric acid is the *dextro-rotatory tartaric acid*; it forms colourless crystals, stable in the air, with a pleasant acid taste, and soluble in water and alcohol. It is a moderately strong acid with the dissociation constant (for the first stage) $0.97.10^{-3}$ at 25°. Its aqueous solutions contain, even when very dilute undissociated molecules in preponderance and comparatively smaller quantities of hydrogen tartrate *ions*; on the other hand, the solutions of its salts undergo extensive dissociation and contain *tartrate ion*, $C_4H_4O''_6$, when it is a case of the neutral salts, and *hydrogen tartrate ion*, $HC_4H_4O_6'$, when hydrogen tartrates are in question Tartrate ion combines readily with metal ions, *e.g.* ferrous and ferric ions, also the ions of aluminium, chromium, manganese cobalt, nickel, lead, copper, and antimonyl ion, further with borate molybdate ion and others, to form complex ions.

Tartaric acid is only slightly soluble in ether (100 : 0·1, according to E. Bourgoin). It does not lose water when heated at 100°; it melts at 167° to 170°, and at a higher temperature is carbonised and emits a quite characteristic odour similar to that of burnt sugar.

3. Of the *tartaric acid salts* (*tartrates*) those of the alkali metals as also a few others (*e.g.* aluminium tartrate and ferric tartrate) are soluble in water. When evaporated on the water bath to the thickness of syrup, a basic salt separates from the solution of ferric

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[1] By optical activity is understood the property of a substance to divert a beam of polarised light, transmitted directly through it or its solution, through a definite angle. "Direct" polarised light is that in which the electro-magnetic waves vibrate continuously only in *one* plane, whilst in the case of ordinary light the waves follow one another at quite a short interval in all possible planes in the path of the beam of light, so that the impression is conveyed to our eyes that all the vibrations take place simultaneously in all the planes.

[2] This is the angle through which the beam of polarised light is rotated when it is transmitted through a layer of a solution 1 dcm. in length, which contains dissolved in one c.c. 1 grm. of the optically active substance.

tartrate in the form of a powder. All the salts which are insoluble in water are dissolved by hydrochloric or nitric acid. Many of the tartrates which alone are insoluble in water or only dissolve with difficulty form, with alkali tartrates, double salts, soluble in water. When ignited, the tartrates are decomposed, with the separation of carbon, and emit the same odour as the free acid.

4. On adding to a solution of tartaric acid or to that of an alkali tartrate a solution of not too great a quantity of a *ferric* or *aluminium salt* and then *ammonia* or *potassium hydroxide*, no precipitation of ferric hydroxide or aluminium hydroxide will take place, as tartrate ion combines with ferric ion or aluminium ion to form *complex ions*, which can neither be decomposed nor precipitated by hydroxyl ion. The precipitation of several other hydroxides by means of alkali hydroxide is also prevented by tartaric acid (also by citric acid, malic acid, etc.).

5. Free tartaric acid yields with the solution of a **potassium salt,** preferably **potassium acetate,**[1] a precipitate of *potassium hydrogen tartrate* (argol), $COOH\,CH(OH).CH(OH).COOK$. This process takes place on adding *potassium acetate* and *acetic acid* to a neutral tartrate dissolved in water until the reaction is decidedly acid. Potassium hydrogen tartrate dissolves readily in alkali hydroxide solutions and mineral acids; tartaric acid and acetic acid do not increase its solubility in water. Alkaline solutions must, therefore, be acidified with acetic acid, and mineral acid solutions either treated with a *sufficient* quantity of ammonium acetate solution (reduction of the concentration of hydrogen ions, see p. 23) or neutralised with alkali and then acidified with acetic acid. The separation of the tartrate precipitate is considerably promoted by shaking, or rubbing the sides of the vessel. If the reaction is to be sensitive, the tartaric acid solution should be strongly concentrated. The addition of an equal volume of alcohol increases the sensitiveness. In the presence of boric acid, the reaction only appears if potassium fluoride is used instead of potassium acetate. The fluorine ion then combines with the boric acid to form a complex ion, and so prevents the formation of a complex borotartrate ion, which gives no precipitate with potassium ion (Barfoed).

6. **Calcium chloride solution** added in excess[2] precipitates

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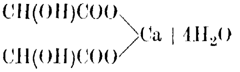
[1] If *concentrated* solutions of potassium acetate are used, there may be no precipitate (Magnier de la Source, *Zeitsch. anal. Chem*, **35**, 586).

[2] Potassium or sodium tartrate solution dissolves calcium tattrate (also other salts which are insoluble in water, *e.g.* calcium phosphate, barium sulphate, etc.); the reactions, which depend on the separation of calcium tartrate,

calcium tartrate from a solution of *neutral* tartrates, in the form of a *white precipitate.*



$$\begin{matrix} CH(OH)COO \\ CH(OH)COO \end{matrix}\!\!>\!Ca + 4H_2O$$

In the presence of ammonium salts, this precipitate is only formed after some time (often a long time); its separation is promoted by shaking or by rubbing the sides of the vessel. The precipitate is always *crystalline*, or at least becomes so after some time; *it dissolves to a clear liquid in not too dilute cold potassium or sodium hydroxide solution*, which should be fairly free from carbonate ion, and should, therefore, be freshly prepared for the purpose. *If this liquid is boiled, the dissolved calcium tartrate separates in the form of a gelatinous precipitate.*[1] The solution becomes clear again when cold.

7. *Calcium chloride solution* in large excess[2] also produces in a solution of tartaric acid or of tartrates, *acidified* with acetic acid, especially after short standing, a copious crystalline precipitate (W. Fresenius).[3] Further, calcium acetate solution in sufficient excess[4] gives both with a 1 per cent. solution of tartaric acid and with dilute acetic acid solutions of tartrates, within a few minutes, a crystalline precipitate of *calcium tartrate*. If the tartaric acid solution is only of 0.1 per cent. strength, the precipitation will only take place after two or three hours if the sides of the vessel are not rubbed; in still more dilute solutions it does not take place at all. If a *few drops* (not more) of a very dilute solution of *l-tartaric* acid or of *ammonium l-tartrate*[5] are added to a solution of *d*-tartaric acid which has remained clear after being treated with calcium acetate, the liquid is *rendered turbid by a silky precipitate* after a few seconds if not at once, and, in the case of very dilute solutions, after long standing. This precipitate consists of the almost insoluble *calcium salt of the (d-+l)-tartaric acid* or *racemic acid* (calcium racemate, $C_4H_4O_6Ca+4H_2O$). A large excess of the precipitant should be avoided, as otherwise calcium *l*-tartrate is precipitated, the

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may, therefore, only occur after the addition of a sufficient quantity of calcium ion to precipitate completely all the tartrate ion present.

[1] According to our experience, the re-precipitation of the precipitate (with the yellow coloration of the solution) sometimes does not occur for reasons not yet discovered.

[2] *Cf.* footnote 2, on p. 499.

[3] *Zeitsch. anal. Chem.*, **38**, 33.

[4] See footnote 2, on p. 499.

[5] For the preparation of *l*-tartaric acid, see Markwald, *Ber.*, **29**, 42; and for that of its ammonium salts, Brönsted, *Zeitsch. anal. Chem.*, **42**, 18.

prismatic crystals of which may in any case be easily distinguished under the microscope from the globular aggregates or sheaves of needles of racemate (see the illustrations in Haushofer, *Mikroskopische Reaktionen*, pp. 86 and 84). The presence of aluminium ion or ferric ion, as also of antimony ion, in considerable quantities prevents the reaction (complex ions). *l*-Tartaric acid may be detected by means of *d*-tartaric acid by the application of the same principle. Further, this method affords a means of distinguishing between the two optically active modifications of tartaric acid (J. N. Brönsted,[1] A. Kling[2]).

8. **Lime water** added in excess[3] produces in solutions of neutral tartrates, or also in a solution of free tartaric acid, if added until the reaction is alkaline, white precipitates which are at first flocculent but later become crystalline, and which while still flocculent are readily dissolved by a solution of tartaric acid or of ammonium chloride. Calcium tartrate is deposited again on the sides of the vessel from these solutions, after several hours, in the form of small crystals

9. *Calcium sulphate solution* added in excess[3] does not produce a precipitate in a solution of tartaric acid, and only a slight one after some time in a solution of a neutral alkali tartrate.

10. When even a very small quantity of calcium tartrate is treated in a test-tube with ammonia solution, a small fragment of crystallised *silver nitrate* added, and the whole slowly heated, the sides of the tube will become covered with a brilliant *film of metallic silver;* if heated quickly, or if dissolved silver nitrate is used, the reduced silver will separate in the form of powder (Arthur Casselmann).

11. *Silver nitrate solution* does *not* give a precipitate with solutions of free tartaric acid, but gives a *white* precipitate with neutral tartrate solutions. The precipitate produced by the falling drops at first disappears, but separates again on vigorous shaking, and on the addition of more silver nitrate. The precipitate, $C_4H_4O_6Ag_2$, dissolves readily in nitric acid and in ammonia solution; when boiled it at once becomes black, owing to the reduced silver. On redissolving the white precipitate (obtained by adding an excess of silver nitrate solution to a neutral tartrate solution) by means of ammonia solution in not too great excess, adding a little sodium hydroxide solution, placing the test-tube in a beaker containing

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[1] *Zeitsch. anal. Chem.*, **42**, 15.

[2] *Ibid.*, **50**, 122.

[3] See footnote 2, on p. 499.

water at about 70° and heating the latter to boiling point, a *mirror-like deposit of silver* will be formed. The success of the reaction is promoted if the test-tube is previously well cleaned, and in particular freed from fat by rinsing it with ether.

12. *Lead acetate solution* gives a white precipitate with a solution of tartaric acid and its salts. The washed precipitate, $(CHOH.COO)_2Pb$, dissolves readily in nitric acid and in ammonia solution free from carbonate.

13. On adding to a solution of free tartaric acid or to that of an alkali tartrate a *small* quantity of *ferrous chloride* or *ferrous sulphate solution*, then one or two drops of *hydrogen peroxide solution* or a few grains of *sodium peroxide*, and finally an excess of *potassium or sodium hydroxide solution*, a *fine violet coloration* will appear. The reaction is not very sensitive, but affords a means of distinguishing tartaric acid from citric acid, malic acid, and succinic acid (Fenton).

14. If tartaric acid or a tartrate is heated on the water bath in a test-tube (previously cleaned with concentrated sulphuric acid) with about 10 parts by volume of concentrated *sulphuric acid*, a *brown coloration* of the sulphuric acid will appear simultaneously with the evolution of gas. (Distinction from citric acid.)

15. If a saturated solution of *potassium dichromate* is poured over a tartaric acid crystal at the ordinary temperature, the zone surrounding the tartaric acid will become *purple-violet to black*, with the liberation of carbon dioxide. (Method of detecting tartaric acid in citric acid, since the latter turns coffee-coloured, although slowly. Caillett.) The reaction may also be carried out with an aqueous solution of tartaric acid. This is treated with dilute sulphuric acid, one or two drops of a solution of potassium chromate or dichromate added, and the whole heated for a short time, whereby the yellow colour is changed into the bluish-violet one of a chromic salt solution (Salzer).

16. On treating a solution of *ammonium molybdate* (previously treated with ammonia until the reaction is slightly acid) with a *little tartaric acid*, adding one or two drops of *hydrogen peroxide* or a trace (not more) of *sodium peroxide*, and gently heating this mixture on the water bath for some time at 60°, the colour, yellow at first (p. 388, 10), will change to *green* and then *blue* (Crismer).

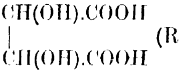
17. If a few drops of a solution of **resorcinol in concentrated sulphuric acid** (about 1 : 100) are added to a little solid tartaric acid or a tartrate, and carefully heated until sulphuric acid vapours just

begin to escape (at about 130° to 140°), the liquid will have a fine wine-red colour (resorcinol tartreinc). The smallest quantity of tartaric acid may be detected by this reaction (E. Mohler).[1] The presence of nitrates, nitrites, chlorates, and other oxidising agents disturbs the reaction (G. Denigès).[2] It is, therefore, not so suitable as a direct test for the presence of tartaric acid or tartrates in mixtures, as for determining whether precipitates, obtained *e.g.* according to Nos. 5 to 8, are actually derived from tartaric acid (*cf.* however, also Sec. 110, 12).

18. With regard to the *microchemical detection* of tartaric acid, see Haushofer, p. 85; and Behrens, Vol. 4, p. 49.

SEC. 135.

(c) **Racemic acid** (Racemate ion, $C_4H_4O''_6$).



$$\begin{array}{l} CH(OH).COOH \\ | \\ CH(OH).COOH \end{array}$$

Crystallised racemic acid has the formula: $(CH)_2(OH)_2.(COOH)_2+2H_2O$ (*cf.* Sec. 134, 1). Its water of crystallisation escapes slowly on exposure to the air, rapidly at 100°. (Distinction from tartaric acid.) Racemic acid behaves like tartaric acid towards solvents. The *racemic acid salts* (racemates) also show a similar behaviour to those of tartaric acid. Several, however, differ from the corresponding tartrates as regards their content of water, their form and solubility. Aqueous solutions of racemic acid and its salts have no rotatory action on a beam of polarised light. (Distinction from tartaric acid.) *Calcium chloride* precipitates from the solutions of the free acid, as from its salts, calcium racemate, $[CH(OH).COO]_2Ca+4H_2O$, as a white crystalline powder (Sec. 134, 7). This is precipitated from its solution in hydrochloric acid at once, or at least very soon, by means of ammonia solution. (Distinction from tartaric acid.) It dissolves in potassium or sodium hydroxide solution, and is re-precipitated on boiling. (Distinction from oxalic acid.) *Lime water* in excess produces at once a white precipitate, which does not dissolve in ammonium chloride solution or in acetic acid. (Distinction from tartaric acid.) *Calcium sulphate solution* does not produce a precipitate at once in a solution of racemic acid (distinction from oxalic acid), but after 10 to 15 minutes calcium racemate separates (distinction from tartaric acid); the precipitate is formed immediately in solutions of neutral racemates. Racemic acid behaves towards *potassium ion* like tartaric acid. If sodium ammonium racemate or sodium potassium racemate is allowed to crystallise, two kinds of rhombic hemihedric crystals are obtained; those which *inter alia* show the surfaces of right sphenoids, and those which show the surfaces of left sphenoids, which stand in relation to one another as an object and its reflection (enantiomorphism). The one kind is the salt of ordinary tartaric acid, the other that of the *l*-tartaric acid (Sec. 134, 1). If the two kinds of crystals are re-dissolved together, the solution will again show the reactions of racemate ion. When a solution of tartaric acid is innoculated with the spores of the mould fungus *pencillium glaucum*, the *d*-tartaric acid is decomposed biologically, and there finally remains only the *l*-tartaric acid. With regard to the microchemical detection of racemate ion, see Haushofer, p. 82.

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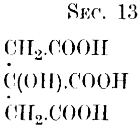
[1] *Zeitsch. anal. Chem.*, 30, 620.

[2] *Chem. Zentr.*, 1895, II., 256.

SEC. 136.

(d) **Citric acid** (Citrate ion, $C_6H_5O'''_7$)



$$\begin{array}{l} CH_2.COOH \\ \quad\cdot \\ C(OH).COOH \\ \quad\cdot \\ CH_2.COOH \end{array}$$

1. Crystallised citric acid, as obtained on cooling its solution, contains water of crystallisation, and has the formula : $C_6H_8O_7+H_2O$. It crystallises in colourless and odourless transparent crystals with a pleasant and very sour taste, dissolves easily in water and alcohol, but with more difficulty in ether (2 26 : 100), effloresces slowly in the air, and loses (if powdered) its water of crystallisation when slowly heated at 55° (Salzer) ; it melts when more strongly heated, and then carbonises while giving off pungent acid vapours, the odour of which it is easy to distinguish from carbonised tartaric acid. An aqueous solution of citric acid is optically inactive. Citric acid is a moderately strong acid (dissociation constants $0.82.10^{-3}$ at 25°); it is therefore somewhat weaker than tartaric acid, and is to a great extent contained in aqueous solution in the form of undissociated molecules.

2. The *citrates* of the alkalis, both the normal and the hydrogen citrates, are readily soluble in water ; no precipitate, therefore, is formed in citric acid solution by means of potassium acetate. The salts of citric acid with weak basic metal ions, *e.g.* with ferric ion, also dissolve readily in water. When evaporated on the water bath to the thickness of syrup, a solution of ferric citrate does not yield a deposit of solid salt. Citrate ion (in the same way and for the same reason as tartrate ion) prevents the precipitation of ferric hydroxide, aluminium hydroxide, etc., by means of alkali hydroxide. It also forms complex ions with other cations, *e.g.* chromium, manganese, and copper ions, and with anions, *e.g.* molybdate ion and tungstate ion. The citrates are dissociated to a normal extent in aqueous solution, but no considerable hydrolysis takes place at this stage. As a tribasic acid, citric acid forms three series of salts ; in addition,

two forms of different isomeric structure are also possible in the case of the mono- and the dihydrogen salts. There is accordingly a corresponding number of different anions of citric acid.

3. *Calcium chloride solution* does not yield a precipitate in a solution of citric acid, either at the ordinary temperature or when boiled. If, however, a somewhat concentrated solution of citric acid is neutralised after the addition of an equivalent or only slightly predominating quantity of **calcium chloride**[1] with **sodium** or **potassium hydroxide,** there will at once result a precipitate of *neutral calcium citrate*, $(C_6H_5O_7)_2Ca_3+4H_2O$, which dissolves readily in the presence of excess of citrate ion, but with more difficulty if an excess of calcium ion is present. It is not dissolved by potassium or sodium hydroxide solution, but is readily soluble in ammonium chloride solution. If the solution obtained by adding not too much ammonium chloride is boiled, calcium citrate of the same composition separates in the form of a white crystalline precipitate, which is no longer soluble in ammonium chloride solution. If a citric acid solution, mixed with calcium chloride, is neutralised, as mentioned above, with ammonia, or if *ammonium chloride, calcium chloride, and ammonia are added to a solution of an alkali citrate*, a precipitate will be formed after several hours standing in the cold, or on the addition of alcohol. If, however, the clear liquid is boiled, and the evaporating ammonia replaced, calcium citrate with the above-mentioned properties will suddenly separate. On heating calcium citrate with ammonia and silver nitrate, no silver will separate, or only a slight quantity.

4. **Lime water** added in excess[1] produces no precipitate in a solution of citric acid or of a citrate in the cold. The reaction should be carried out in a closed flask. If the solution, however, is boiled with a fair excess of lime water (prepared with hot water) a *white precipitate of calcium citrate* is formed, which, when cooled and occasionally shaken in a closed flask, will partly, and after some time, completely disappear.

5. **Barium acetate solution** gives, when added in excess to a solution of an alkali citrate, whether hot or cold, an amorphous precipitate with the formula: $(C_6H_5O_7)_2Ba_3+7H_2O$. The same precipitate is produced when a citric acid solution is treated with

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[1] The addition of citrate ions in excess effects the solution of calcium citrate and of many other compounds insoluble in water (calcium phosphate, calcium oxalate, etc.); the reactions given in 3 and 4, which are based on the separation of calcium citrate, only succeed, therefore, when sufficient calcium ion is added as is necessary for the precipitation of all the citrate ion present.

an excess of baryta water. The precipitate is not produced in dilute solutions in the cold, because it is not insoluble in water; if heated, however, an amorphous precipitate separates, which soon changes into a salt with the formula: $(C_6H_5O_7)_2Ba_3+5H_2O$, consisting of microscopic needle-shaped crystals. If this salt, or the amorphous precipitate, is heated for about two hours on the water bath with excess of a solution of barium acetate, another very characteristic salt is formed. This consists of small, well-formed, monosymmetrical splinters, and has the formula: $(C_6H_5O_7)_2Ba_3+3{\cdot}5H_2O$. In the case of very dilute solutions the salt is only formed after concentration. The microscopical appearance of these crystals is a certain proof of their identity (H. Kammerer [1]).

6. On adding *lead acetate solution* in excess to a solution of citric acid, a white amorphous precipitate of *lead citrate* is produced, which dissolves readily after washing in ammonia solution free from carbonate. After being digested for some hours with water or acetic acid on the water bath, the precipitate becomes crystalline, and then has the formula: $(C_6H_5O_7)_2Pb_3+3H_2O$. It does not produce well-formed, microscopic crystals. If a solution of citric acid or a citrate is treated with about $\frac{1}{10}$ of its volume of glacial acetic acid, and a similar quantity of saturated lead acetate solution, a white milky turbidity will be produced by the lead acetate, which dissolves on boiling and reappears on cooling (Möslinger [2]).

7. *Silver nitrate* precipitates silver citrate, $C_6H_5O_7Ag_3$, as a white flocculent precipitate from solutions of neutral alkali citrates. On boiling a sufficient quantity of this with only a little water, a gradual decomposition will take place, with the separation of silver.

8. On heating citric acid or a citrate with *concentrated sulphuric acid* on the water bath in a test-tube cleaned with concentrated sulphuric acid, *carbon monoxide* will escape first, then *carbon dioxide* and *acetone*. The sulphuric acid only turns *lemon-yellow*, even after being heated for half an hour (E. Schmidt, Pusch); the solution only becomes dark after long boiling, when sulphur dioxide escapes.

9. If 5 c.c. of a 1 or 2 per cent. solution of citric acid or of a citrate are heated to boiling point with 1 c.c. of **mercuric sulphate solution** (prepared from 5 grms. of mercuric oxide, 20 c.c. of concentrated sulphuric acid, and 100 c.c. of water) and, after the removal of the flame, treated drop by drop with 2 per cent. **potassium permanganate solution,** decolorisation takes place and a white precipitate

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[1] *Zeitsch. anal. Chem.*, **8**, 298 (with illustration of the crystals).

[2] *Zeitsch. anal. Chem.*, **38**, 719.

is formed. The reaction depends on the fact that the citric acid is oxidised to *acetone dicarboxylic acid*, $CH_2(COOH).CO.CH_2(COOH)$, which at the moment of its production is precipitated as a very sparingly soluble mercuric double salt (complex compound of a basic mercuric salt with mercuric acetone dicarboxylate) (G. Denigès[1]).

10. If the **oxidation** is carried out with **potassium permanganate** in the absence of mercuric sulphate, *acetone dicarboxylic acid* is also obtained, which then remains in solution, but which may be detected by conversion into pentabromacetone, $CBr_3.CO.CHBr_2$, and then into bromoform, $CHBr_3$. On dissolving, *e.g.* about 0·01 grm. of citric acid in 1 c.c. of water, adding a few drops of 0·3 per cent. potassium permanganate solution, heating (but not boiling) the mixture until the red coloration has disappeared, and then treating it with 3 to 5 drops of saturated bromine water, a turbidity or white precipitate will be formed either at once or on cooling. On the addition of sodium hydroxide solution, the well-known odour of bromoform will be noticed (L. Stahre,[2] A. Wöhlk[3]). R. Kunz[4] recommends the following method of applying the test: 10 c.c. of the solution under examination are treated with 1 c.c. of dilute sulphuric acid (1 : 1) and with 0·3 c.c. of potassium bromide solution (22·5 grms. in 100 c.c.). After the liquid has been shaken, 1 c.c. of 5 per cent. potassium permanganate solution is introduced, the whole well shaken, and the test-tube placed in a water bath heated to 40° to 45°. The manganese dioxide hydrate which first separates gradually dissolves again. After about 5 minutes the last particles of it are removed, as also the elementary bromine liberated from the potassium bromide, by means of the addition drop by drop of a saturated ferrous sulphate solution acidified with a little sulphuric acid, and, after placing the tube in cold water, the white turbidity of pentabromacetone will be observed. If allowed to stand over-night it subsides as a crystalline deposit. (Distinction from tartaric acid, malic acid, succinic acid, lactic acid.)

11. When citric acid or a citrate is heated with *concentrated* sulphuric acid by placing the test-tube containing the mixture in a boiling water bath, *acetone dicarboxylic acid* is also formed, which may be detected by means of the following so-called Legal's test. On carefully diluting the mixture when cold with water, rendering it alkaline with sodium hydroxide solution and treating it when

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[1] *Zeitsch. anal. Chem.*, **38**, 719.

[2] *Ibid.*, **36**, 195.

[3] *Ibid.*, **41**, 77.

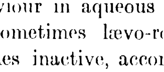
[4] *Ibid.*, **54**, 126.

cool with a few drops of freshly-prepared sodium nitroprusside solution, a *ruby-red coloration* will appear, which changes to *pinkish-violet* when treated with glacial acetic acid in excess (B. Merk[1]).

12. On introducing citric acid (at least 0·01 grm.) with an excess of *ammonia solution* (3 c.c.) into a strong glass tube fused together at the bottom, and then fusing the tube in such a way that only a small space remains free above the liquid, heating it for six hours at 110° to 120°, and then pouring the liquid, when cold, into a shallow porcelain dish, an *intense blue or green product* will be obtained when it has stood for some hours in the light and air. (Distinction of citric acid from oxalic, tartaric, and malic acids, and method for detecting small quantities of it in the presence of these acids. Sarandinaki, Sabanin, and Laskowsky.[2]) These colorations, which are characteristic of citric acid, are also obtained when the acid is heated with a little undiluted glycerin (0·7 part) at a very low temperature until the mass begins to bubble, the residue dissolved in ammonia solution, the greater portion of the liquid evaporated, and then a little water and two drops of red fuming nitric acid diluted with 5 times its quantity of water added. The colour, green at first, changes into blue by the action of heat on the water bath (Mann). The reaction also occurs when, instead of nitric acid, a small quantity of hydrogen peroxide solution is added.

13. With regard to the *microchemical detection* of citric acid, see also Haushofer, p. 75; and Behrens, Vol. 4, p. 51.

SEC. 137.



(e) Malic acid, $\begin{array}{l} CH(OH).COOH \\ | \\ CH_2.COOH \end{array}$ (Malate ion, $C_4H_4O''_5$).

1. *Malic acid* is known in three stereoisomeric forms: *d*-malic acid or dextro-rotatory malic acid, *l*- or lævo-rotatory malic acid, and "racemic," inactive $(d+l)$-malic acid. They are only distinguished from one another by their optical activity. The *ordinary malic acid*, prepared from fruit juice, is *l*-malic acid; as in the case of its salts, its behaviour in aqueous solution towards a polarised beam of light is sometimes lævo-rotatory, sometimes dextro-rotatory, and somtimes inactive, according to its temperature and concentration; in the presence of uranyl salts the lævo-rotation in alkaline solution increases to a degree of 450 times the original

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[1] *Zeitsch. anal. Chem.*, **44**, 124.

[2] *Ibid.*, **17**, 73.

value (P. Walden[1]). Beryllium salts behave in a similar manner. The ($d+l$)-malic acid is obtained by synthetic preparation. Malic acid is a moderately strong acid; it is weaker than citric acid, and is therefore present in its aqueous solutions to a great extent as undissociated molecules. (Dissociation constant 3.9.10^{-3} at 25°.) Malic acid is about twenty times as strong as acetic acid.

2. *Ordinary malic acid* crystallises with difficulty in crystalline layers or sheaves of associated needles, which deliquesce in the air, are dissolved readily by water and alcohol and slightly by ether, and melt at about 100°. When heated at 100° in the air, or in a vacuum at a higher temperature, anhydrous acids are produced in preponderance. If heated for some time at 140° to 150° malic acid is converted mainly into *fumaric acid*, $C_2H_2(COOH)_2$, while water escapes. Heated at temperatures between 150° and 200° in a glass tube or small retort, malic acid gives a residue of fumaric acid, while water and maleic anhydride, $C_2H_2(CO)_2O$, distil. The latter combines in part with water to form maleic acid, $C_2H_2(COOH)_2$, which is stereoisomeric with fumaric acid. When heated at over 200° the fumaric acid volatilises partly undecomposed. The resulting crystalline sublimates, which form in the glass tube above the heated part or in the neck of the retort, are *very characteristic* of malic acid. When heated with nitric acid, malic acid readily yields oxalic acid, with the evolution of carbon dioxide.

3. Malic acid forms, with most cations, salts which are soluble in water, and which are dissociated in aqueous solution to a normal degree; a considerable hydrolysis does not take place at this stage. As a dibasic acid, malic acid forms two classes of salts, normal malates and hydrogen malates, the solutions of which contain accordingly *malate ion*, $C_4H_4O''_5$, or *hydrogen malate ion*, $C_4H_5O'_5$. Potassium hydrogen malate ion dissolves fairly readily in water; malic acid is, therefore, not precipitated from its solution by potassium acetate solution. Malic acid, like tartaric acid, prevents the precipitation of ferric hydroxide, etc., by means of alkalis. Further, malic acid frequently shows a tendency to form complex ions.

4. On adding **calcium chloride,** ammonium chloride, and ammonia solution in excess to a solution of malic acid or of an alkali malate, *the liquid remains clear*. and *no precipitation takes place* (if the quantity of ammonium chloride was not too small) *even on prolonged* boiling (distinction from citrate ion); if, however, two or three volumes of alcohol are added, *calcium malate*, $C_4H_4O_5Ca+3H_2O$, will separate

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[1] *Ber.*, **30**, 2889.

as a white flocculent precipitate. If the liquid is previously heated nearly to boiling point, and just sufficient hot alcohol to cause a precipitation added, the precipitate will adhere to the sides of the glass tube in the form of soft lumps, which harden on cooling, and by means of pressure may be broken up into a crystalline powder (Barfoed). When heated with ammonia solution and *silver nitrate solution*, calcium malate does not cause a separation of silver, or only a slight one. Calcium malate dissolves in boiling lime water. (Distinction and method of separation from calcium citrate. Fleischer.)

5. **Lime water** does not precipitate malate ion, either from a solution of free malic acid, or from that of a malic acid salt. Even on boiling, the liquid will remain perfectly clear, provided the lime water was prepared with boiling water.

6. *Lead acetate solution* produces a white precipitate of *lead malate*, $C_4H_4O_5Pb+3H_2O$, in a solution of malic acid, or of the malates. The precipitation is most complete when the liquid is neutralised with ammonia solution, since the precipitate is somewhat soluble, even in the case of a low concentration of hydrogen or hydroxyl ions. On heating the liquid, in which the precipitate is suspended, to boiling point, a portion dissolves, whilst the remainder melts and under water resembles fused rosin. The salt separates from the hot solution, when cooled, in the form of small needles or flakes. If it is a question of fusing lead malate in small quantities, it should first be heated until the precipitate has agglomerated, the greater portion of the liquid poured off, and the remainder heated to boiling point with the precipitate. This reaction is only decisive if the lead malate is fairly pure; if it is mixed with other lead salts, or if ammonia, for example, is added until the liquid is alkaline, the reaction will not occur, or only incompletely.

7. *Silver nitrate solution* produces in solutions of neutral alkali malates a white precipitate of silver malate, $C_4H_4O_5Ag_2$, which becomes grey after long standing, or when boiled.

8. *By oxidation with potassium permanganate, aceto-oxalic acid*, $COOH.CO.CH_2.COOH$, is formed, the mercuric salt of which dissolves readily in dilute sulphuric acid, but with difficulty in acetic acid. On heating a solution of malic acid or of a malate to boiling point, after the addition of mercuric acetate solution (prepared by dissolving 5 grms. of the salt in 100 c.c. of water and adding 1 c.c. of glacial acetic acid), then filtering the liquid to remove any turbidity which may have formed, and adding drop by

drop 2 per cent. potassium permanganate solution, a white precipitate will immediately be produced. If mercuric *sulphate* is used instead of the acetate, the reaction will not appear. (Distinction from *citric acid.* G. Denigès.[1])

9. If malic acid is heated on the water bath with *concentrated sulphuric acid, carbon dioxide,* and *carbon monoxide* will be evolved first, then the liquid will become brown and black, with the evolution of *sulphur dioxide.*

10. With regard to the *microchemical detection* of malic acid, see Haushofer, p. 67; and Behrens, Vol. 4, p. 17.

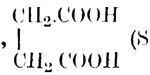
SECOND DIVISION

Of the First Group of Organic Acids.

The acids of the second division can be sublimed, whereby they are partially converted into acid anhydrides (succinic acid). They are not oxidised by nitric acid, and are appreciably soluble in ether, although succinic acid dissolves with comparative difficulty. They are precipitated from solutions of their normal alkali salts by neutral ferric chloride solution: *Succinic acid, cinnamic acid.*[2]

SEC. 138.

(a) Succinic acid, (Succinate ion, $C_4H_4O''_4$).



$$\begin{array}{l} CH_2.COOH \\ | \\ CH_2.COOH \end{array}$$

1. *Succinic acid* is a weak acid (dissociation constant $6.6.10^{-3}$ at 25°), and its solutions only undergo electrolytic dissociation to a slight degree. It crystallises in colourless and odourless rod-like or flat crystals. It dissolves in 146 parts of water at 20°, dissolves readily in hot water and hot alcohol, sparingly in cold alcohol, and slightly in ether (1 265 : 100). When heated for some time at 140° it partly sublimes undecomposed and partly yields water and succinic anhydride, which can be sublimed. If heated rapidly, the acid melts at 181° and boils at 235°, whereby it is to a great

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[1] *Zeitsch. anal. Chem.*, **40**, 122

[2] Cinnamic acid is closely related in many respects in its analytical behaviour to the second group of organic acids (especially to those of the first division of it); it forms to a certain extent a transition stage in passing from the first to the second group.

extent decomposed into anhydride and water. The sublimed anhydride consists of glistening needles. Heated in the air, succinic acid burns with a blue smokeless flame. When pure it is odourless, and has a slightly acid taste. It is not decomposed when heated with nitric acid. It also remains unchanged when heated with neutral potassium permanganate solution or, if pure acid is present, also in the presence of sulphuric acid (C. von der Heide and H. Steiner[1]).

2. The *succinic acid salts* (succinates) are decomposed on ignition, those with alkali ions or the ions of the alkaline earths being converted into carbonates, with the separation of carbon. Many of the succinates are soluble in water; they are dissociated to a normal extent in aqueous solution, but no considerable hydrolysis takes place at this stage. As a dibasic acid succinic acid forms two series of salts: normal succinates and hydrogen succinates, the solutions of which correspondingly contain *succinate ion*, $C_4H_4O''_4$, and *hydrogen succinate ion*, $C_4H_5O'_4$. Both sodium succinate and sodium hydrogen succinate may easily be obtained pure, even from very impure liquids, since they are only slightly soluble in alcohol and crystallise readily; they may, therefore, be used for the detection and separation of succinic acid.[2] On heating succinates with potassium hydrogen sulphate in a small tube, succinic anhydride sublimes. Further, the acid may also be obtained from the salts by decomposition with sulphuric acid and extraction with hot absolute alcohol, also practically all the succinic acid may be obtained in ethereal solution by means of repeated extraction by shaking solutions (strongly acidified with sulphuric acid) with ether—or, better, by continuous extraction in a suitable apparatus (*cf.* p. 47).

3. On adding **calcium chloride,** ammonium chloride, and ammonia solution in excess to a solution of succinic acid or an alkali succinate, the liquid will remain clear in the cold, or, if the quantity of ammonium chloride was not too small, also when boiled. On adding 2 or 3 volumes of alcohol (86 per cent. by weight), however, *calcium succinate*, $C_4H_4O_4Ca+3H_2O$, will separate in a crystalline form, although often only after some time.

4. *Barium chloride solution* produces in solutions of alkali succinates, but not in that of free succinic acid, a crystalline white precipitate of *barium succinate*, $(CH_2)_2.(COO)_2Ba$, though, as a rule, only after some time. Heat promotes the separation. On

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[1] *Zeitsch. anal. Chem.*, **51**, 70.

[2] *Cf.* Meissner and Jolly, *Zeitsch. anal. Chem.*, **4**, 502.

adding alcohol the precipitate rapidly separates from dilute solutions.

5. **Ferric chloride solution,** prepared by dissolving 1 part of crystallised ferric chloride in 1 part of cold water and then diluting with 8 parts of cold water (or by treating ordinary ferric chloride solution with *dilute* ammonia solution until a turbidity appears and then filtering the liquid), produces in neutral solutions of succinates a gelatinous precipitate (at first pale, then brownish-red), the composition of which corresponds to the formula $(CH_2)_2(COO)_2Fe(OH)$. The precipitate dissolves in a large excess of the precipitant, forming a reddish-brown solution; the precipitation does not take place, therefore, in very dilute succinate solutions. The presence of anions which tend to form complexes with ferric ion disturbs the reaction, *e.g.* oxalate, tartrate, citrate, malate, and acetate ions. In that event, no precipitate is obtained or a paler one than usual. The precipitate dissolves easily in mineral acids, but sparingly in cold acetic acid; it is decomposed by ammonia solution, whereby succinate ion dissolves and a less gelatinous, darker residue remains, which is less soluble and contains more iron (O. Doepping,[1] Barfoed)

6. *Lead acetate solution*, when added drop by drop to a solution of free succinic acid or of alkali succinates, produces an amorphous, white precipitate, which re-dissolves immediately in the presence of an excess of succinate ion or lead ion, but which soon separates from these solutions in a crystalline form. This precipitate, *lead succinate*, $(CH_2)_2(COO)_2Pb$, scarcely dissolves in water, even if boiling, or in succinic acid or lead acetate solutions, is readily soluble in nitric acid, but less easily in acetic acid; when treated with ammonia solution it is converted into a basic salt.

7. *Silver nitrate solution* precipitates succinate ion almost completely from neutral solutions, though often only on standing, as white *silver succinate*, $(CH_2)_2(COOAg)_2$.

8. Succinic acid, when carefully heated at about 200° with *resorcinol* and sufficient *concentrated sulphuric acid* to moisten the mixture thoroughly, yields a brownish-yellow, fused mass, showing a green fluorescence. On adding water, it becomes a yellow, and on being treated with ammonia solution in excess a pale-red solution, with a pronounced green fluorescence (*resorcinol succinein*).

9. With regard to the *microchemical detection* of succinic acid, see Haushofer, p. 73; and Behrens, Vol. 4, p. 43.

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[1] *Liebig's Ann. d. Chem.*, **47**, 279.

SEC. 139.

(b) Cinnamic acid (β-Phenylacrylic acid), $C_6H_5.CH{=}CH.COOH$ (Cinnamylate ion, $C_9H_7O'_2$).

1. *Cinnamic acid* crystallises in monosymmetrical white rods with a melting point of 133°. It boils at 300°. It dissolves with difficulty in cold water (1 part in 3500 parts at 17°), more readily in hot water, and easily in alcohol and ether. It may readily be almost completely extracted from its aqueous solutions by shaking with ether, as also from the solutions of its salts, strongly acidified with sulphuric acid. It is a weak acid (dissociation constant $3.5.10^{-5}$ at 25°); its aqueous solutions, therefore, only undergo slight dissociation. When rapidly heated the greater portion volatilises without decomposition and may be sublimed. It is volatile with steam; it may be almost completely expelled in a current of steam from its solutions or from concentrated solutions of its salts, strongly acidified with sulphuric acid.

It is oxidised by means of potassium permanganate in alkaline solution in the cold to *benzaldehyde*, and, when heated, to *benzoic acid*. When treated with strong nitric acid it is converted into nitrocinnamic acid. Apart from the ordinary cinnamic acid, a *stereoisomeric variety* is known, which differs from it in its chemical behaviour, and stands in the same relation to it as, *e.g.* maleic acid to fumaric acid (*cis-* and *trans-*form). This cis-form appears in three heteromorphous forms, *i.e.* differing only in their melting point and the shape of their crystals: natural isocinnamic acid, allocinnamic acid, and artificial isocinnamic acid.[1]

2. The *cinnamic acid salts* (*cinnamylates*) vary in their degree of solubility. Only those of the alkali metals dissolve easily. The soluble cinnamylates are dissociated to a normal degree in aqueous solution; the sodium salt is appreciably hydrolysed, and its concentrated solutions show an alkaline reaction. On adding a strong *acid* to a cold aqueous solution of a cinnamylate, cinnamic acid will be precipitated at once or after standing for a short while, even in the case of slight concentration (as low as under 0·1 per cent. of cinnamylate ion).

3. **Manganous salt solutions** yield with not too dilute solutions of cinnamylates, although slowly (within an hour), a *white* precipitate of *manganous cinnamylate*, $(C_6H_5.CH:CH.COO)_2Mn+4H_2O$, which

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[1] E. Beilmann, *Ber.*, **42**, 182, 1413; **44**, 3156; C. Liebermann, *Ibid.*, **42**, 1027.

gradually turns yellow and becomes crystalline. (Distinction from benzoic acid.)

4. **Ferric chloride solution,** treated carefully with very dilute ammonia solution until a precipitate begins to form, and then filtered, gives a *yellow* precipitate with solutions of cinnamylates.

5. **Calcium chloride solution** in sufficient excess gives with cinnamylate solutions a *white* precipitate of *calcium cinnamylate*, $(C_6H_5.CH:CH.COO)_2Ca+3H_2O$, which dissolves with difficulty in water (1 part in about 600 parts) but more readily in alcohol.

In dilute solutions (*e.g.* in a 1 per cent. solution of sodium cinnamylate) the precipitation only takes place after shaking. An additional quantity of cinnamic acid may be precipitated from the filtrate of the original precipitate by the addition of hydrochloric acid.

6. *Lead acetate solution* gives with cinnamylate solution a finely pulverulent precipitate of *lead cinnamylate*, $(C_6H_5\,CH:CH.COO)_2Pb$, and *silver nitrate solution* a pulverulent precipitate of *silver cinnamylate*, $C_6H_5.CH:CH.COOAg$, which dissolves readily in ammonia solution.

7. On treating cinnamylate ion in a slightly alkaline solution *in the cold* with a few drops of **potassium permanganate solution** it is oxidised to *benzaldehyde*, which may be detected by its odour of bitter almonds. (Distinction from benzoate ion. C. von der Heide and F. Jakoo.[1])

8. In Mobler's reaction described in connection with benzoic acid (Sec 141, 9), a brownish-red coloration is produced by cinnamylate ion, like benzoate ion ; it differs, however, in that this brownish-red coloration does not disappear on boiling (C. von der Heide and F. Jakob).

9. With regard to the *microchemical detection* of cinnamic acid, see Behrens, Vol. 4, p. 91.

SEC. 140.

Summary and Remarks on Organic Acids.

1. Of the organic acids and their ions dealt with, *oxalic acid* is characterised by the fact that calcium sulphate solution precipitates the free acid or its soluble salts from a solution slightly acidified with acetic acid. If calcium chloride solution is used instead of

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[1] *Zeitsch. anal. Chem.*, **53**, 460. With regard to a similar method of detection by means of photochemical oxidation to benzaldehyde in the presence of uranyl acetate solution, *cf.* A. Jorissen, *Zeitsch. anal. Chem.*, **41**, 630.

calcium sulphate solution, this reaction loses its value as a distinctive test (Sec. 143, 7).

2. Tartaric acid is distinguished by the sparing solubility of potassium hydrogen tartrate, the solubility of its calcium salt in cold sodium and potassium hydroxide solution, its behaviour towards ammonia solution and silver nitrate, the almost complete insolubility of calcium racemate (Sec. 134, 7); further, by the odour which tartaric acid and its salts emit when heated, and finally by the colour reaction with resorcinol and sulphuric acid. It may best be detected in the presence of other acids by means of potassium acetate or potassium fluoride (Sec. 134, 5), as also by testing the previously precipitated calcium salt with resorcinol and sulphuric acid (Sec. 134, 17). The test with potassium acetate is best carried out with a solution concentrated by evaporation; the addition of alcohol should be avoided, since in the presence of alcohol oxalic acid solutions can also give a precipitate (of potassium hydrogen oxalate). Further, the reactions given in Sec. 134, 13, 15, and 16, afford a means of distinguishing tartaric acid from citric acid, malic acid, and succinic acid, and of detecting it in their presence. For the detection of tartaric acid in the presence of citric acid, reaction 14—heating with concentrated sulphuric acid—is suitable (*cf.* also Sec. 136, 8), since by means of this even 0·2 per cent. tartaric acid may be detected in citric acid by the resulting brown coloration. Other organic substances, however, apart from tartaric acid and tartrates, give the same brown coloration, *e.g.* sugar and tannin.[1]

3. *Citric acid* may, as a rule, be recognised by its behaviour to lime water or to calcium chloride and ammonia in the presence of ammonium chloride, but in this case the absence or the previous separation of oxalic acid and tartaric acid, as also the use of a sufficient excess of lime water or a correctly measured quantity of calcium chloride, is assumed. Further, the microscopical appearance of the barium salt (Sec. 136, 5), as also the preparation of the products of decomposition described in Sec. 136, 12, form a reliable and trustworthy means of detection; above all, however, the reactions of Möslinger, Denigès, Stahre, and Merk are important and characteristic.

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[1] With regard to the distinction of tartaric acid from the other organic acids by means of *hexaminocobaltichloride* (luteo-cobalt chloride), *cf.* C. D. Braun, *Zeitsch. anal. Chem.*, **7**, 349. Tartaric acid when heated with the above-mentioned reagent in alkaline solution gives a green to bluish-violet colour reaction, whereas malic acid, formic acid, succinic acid, acetic acid, oxalic acid, and citric acid give precipitates of cobaltic hydroxide under similar conditions.

In Möslinger's test (Sec. 136, 6) the presence of tartaric acid and malic acid has a disturbing influence. Tartaric ion should, therefore, be precipitated as potassium hydrogen tartrate, and the filtrate treated with ammonia to slightly alkaline reaction to separate the malic acid, and barium chloride solution and $\frac{1}{5}$ volume of alcohol added to the new filtrate. After standing for 12 to 18 hours the precipitate, presumably containing barium citrate, is filtered off and without being washed is distributed in about 15 c.c. of hot water and carefully decomposed drop by drop with dilute sulphuric acid. It should be filtered from the barium sulphate, and the filtrate tested according to Sec. 136, 6, by boiling with glacial acetic acid and lead acetate. If the whole of the lead precipitate does not re-dissolve on boiling, the boiling liquid may be filtered and note taken whether the filtrate, on cooling, shows a milky turbidity (J. Schindler [1]). The detection is rendered more trustworthy in the presence of foreign acids by converting the lead precipitate into calcium citrate. The lead precipitate is filtered off when completely cold, washed several times with 50 per cent. alcohol, distributed in water and decomposed by the introduction of hydrogen sulphide. After boiling away the excess of hydrogen sulphide the filtrate from the lead sulphide is rendered slightly alkaline with ammonia solution and treated with a little calcium chloride solution. When this solution is reduced to about 1 c.c. and heated for some time by inserting the test-tube containing it into boiling water, calcium citrate crystals separate, the characteristic shape of which may be recognised under the microscope (J. Mayrhofer).

Denigès' reaction (Sec 136, 9) may, according to recent investigations, be considered as specific for citric acid. If large quantities of tartaric acid are present with citric acid, the solution is first heated with a considerable quantity of potassium permanganate solution until decolorisation takes place; mercuric sulphate solution is then added and the whole boiled.

In the case of Stahre's reaction (Sec. 136, 10) the odour of bromoform may be produced by malic acid but not by tartaric acid. The real characteristic therefore lies in the appearance of the pentabromo-acetone turbidity, which does not occur in the case of malic acid. In the presence of these acids, therefore, bromine water should be added first and then the potassium permanganate solution, the latter in a somewhat larger quantity.

Merk's test (Sec. 136, 11) is affected in the presence of tartaric acid by the dark coloration which the latter produces in concentrated sulphuric acid. In that case, instead of pure sulphuric acid, a mixture of 1 part of acetic anhydride and 2 parts of concentrated sulphuric acid should be used, as there is then no disturbing influence.

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[1] *Zeitsch. anal. Chem.*, **52**, **32**.

4. *Malic acid* would be easily characterised by the behaviour of its lead salt when heated under water if this reaction were more sensitive and if it were not so easily prevented by the presence of other acids. Conversion into oxalic acid (Sec. 137, 8) is characteristic of malic acid. The most certain method of recognising it is by converting it into maleic acid and fumaric acid (Sec. 137, 2). Malic acid may also be distinguished from citric acid and tartaric acid by the sparing solubility of its lead salt in ammonia solution, whereas lead citrate and lead tartrate dissolve easily in ammonia solution free from carbonate. Calcium citrate and calcium malate may be separated by means of boiling lime water, which dissolves the latter and leaves the former undissolved. Malic acid may also be detected in the presence of citric acid and succinic acid by treating the solution (acidified with a few drops of sulphuric acid) with a little potassium dichromate and heating it to boiling point when, in the presence of malic acid, the odour of fresh apples will become noticeable (Papasogli and Poli).

5. *Succinic acid* is above all characterised by its behaviour towards ferric chloride solution. The same may be said of *cinnamic acid*, the behaviour of which towards manganous salt solutions—only oxalate ion gives precipitates apart from cinnamylate ion—and further, its sparing solubility in water and its oxidation to benzaldehyde may be noted. In the presence of *small* quantities of cinnamylate ion those reactions fail which depend on the sparing solubility of the calcium salt and, under certain conditions, on that of free cinnamic acid. In such cases tests for cinnamic acid must be applied to the extract obtained by shaking the solution (acidified with hydrochloric acid) with ether (*cf.* Sec. 145).

6. If *only one* acid or the ion of one of the six acids mentioned is in solution, its behaviour towards lime water affords certain information, for succinate ion and malate ion are not precipitated, whereas citrate ion is only precipitated by continued boiling, and cinnamylate ion, tartrate ion, and oxalate ion are precipitated even in the cold; the precipitate produced by cinnamylate or tartrate ion dissolves on the addition of ammonium chloride, whilst calcium oxalate does not. A definite distinction between succinate ion

and malate ion, as also between cinnamylate ion and tartrate ion, is then afforded by means of the ferric chloride reaction.

7. If it is likely that *several* of the acids mentioned or their ions are *present together* in solution, a test should first be made to ascertain whether a turbidity is produced by the addition of hydrochloric acid.[1] If this is not the case, no notice need be taken of the cinnamylate ion in the following procedure. If, however, a turbidity does appear, which is removed on shaking the liquid with ether, it is not necessarily caused by cinnamic acid; it may well be due to the presence of benzoic or salicylic acid

Apart from the result of this preliminary test, oxalate, tartrate, and any cinnamylate ions are precipitated from the main portion of the solution by the addition of a slight excess of calcium chloride and ammonia solution in the presence of ammonium chloride. It should, however, be noted that under these conditions the calcium cinnamylate is only incompletely precipitated,[2] and the calcium tartrate almost quantitatively precipitated only after some time, possibly after about two hours; also that citrate ion, if present in any quantity, prevents the complete precipitation of the oxalate ion and still more that of the tartrate ion. Calcium tartrate may be extracted from the precipitate by treatment with sodium hydroxide solution (Sec 134, 6). Tartrate ion may also be detected in a portion of the precipitate by means of resorcinol and sulphuric acid (Sec 134, 17). Another portion of the precipitate is boiled with sodium carbonate solution: the solution filtered from the resulting calcium carbonate may, if the result of the preliminary test renders it necessary, be used for the detection of cinnamic acid in accordance with Sec 139, 3, 4 and 7, as also by precipitation of the free acid by means of hydrochloric acid. A second portion of the calcium carbonate filtrate (slightly acidified with acetic acid) is tested for oxalate ion with calcium sulphate solution; a further portion may be used for the detection of tartrate ion by precipitation as potassium hydrogen tartrate, or a precipitate may be produced with calcium acetate solution, and the filtrate of this tested for tartrate ion by means of *l*-tartaric acid (Sec. 134, 7. S. N. Brönsted [3]).

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[1] This may have been observed in the original tests for cations in the detection of the metals of the first division of the fifth group (Sec. 157, 1; Sec. 164, 1).

[2] Hence, in the case of very small quantities, the cinnamic acid will not be found here.

[3] *Zeitsch. anal Chem.*, **42**, 15. In a similar manner the test may, if necessary, be carried out here for *l*-tartaric acid by means of *d*-tartaric acid solution.

When testing for citrate ion, malate ion, and succinate ion, the original filtrate (of the first precipitate produced with calcium chloride solution) is treated with about three times its quantity of alcohol. After standing for several hours, calcium citrate, calcium malate, and calcium succinate (and with them the remainder of the calcium oxalate and tartrate) will then be precipitated. A small portion of the precipitate, after being washed with 70 per cent. alcohol, is tested for citrate ion according to the methods of Denigès, Stahre, or Merk (Sec. 136, 9, 10, 11).

If no citrate ion is detected, the main quantity of the precipitate is tested for malate and succinate ion according to the methods given in the following paragraphs; if citrate ion is present, the main portion of the precipitate is dissolved in a little dilute hydrochloric acid, ammonia solution added to the solution until the reaction is alkaline and the whole then heated until it boils. Calcium citrate separates and can be filtered off; the filtrate may be tested for malate and succinate ions. For this purpose a further quantity of calcium malate and calcium succinate are precipitated by adding 80 per cent. alcohol and allowing the liquid to stand for several hours, care being taken to keep the ammonia in excess.

To test for succinate ion the malate ion is best destroyed by means of oxidation with nitric acid (*cf.* Sec. 176, rubric number 188), or with potassium permanganate.[1] Succinic acid may be extracted from the residues left after oxidation by treating the liquid (strongly acidified with sulphuric acid) with ether in a continuous extraction apparatus, and then identified by means of the reaction with ferric chloride. In the absence of a continuous extraction apparatus the liquid may be *repeatedly shaken* with ether.

As malate ion is oxidised by nitric acid to oxalate ion, the detection of the latter in the product of reaction resulting from the oxidation with nitric acid may be regarded as a proof of the presence of malate ion in the original material.

The *direct* detection of malate ion by the following method is more trustworthy. A portion of the precipitate possibly containing calcium malate is boiled with 10 per cent. sodium carbonate solution, the liquid filtered from the resulting calcium carbonate and the filtrate evaporated to dryness with 10 per cent. sodium hydroxide solution. The evaporation residue is heated for two hours in a drying oven at 120° to 130°, then dissolved in hydrochloric acid and the solution shaken with ether. If malate ion was present the ether will, after evaporation, leave fumaric acid behind, which may be recognised by its sparing solubility in water, and after crystallisation from a drop of water, may be recognised microchemically by its characteristic irregular feathery or branching crystals [1] (R. Kunz and F. Adam [2]).

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[1] Suitable methods for this purpose have been given by C. von der Heide and J. Steiner, *Zeitsch. anal. Chem.*, **51**, 70, and C. von der Heide and E. Schwenk, *Ibid.*, **51**, 529.

One method of detecting *malic acid* in the presence of oxalic, tartaric, and citric acids consists in concentrating the solution of the acids (neutralised by ammonia solution) so far that it begins to crystallise when cold, then neutralising it again when warm with ammonia solution (since, owing to hydrolysis the ammonia escapes during evaporation and the liquid will have become acid again) and treating it with 8 parts of strong alcohol (98 per cent.). After 12 to 24 hours the solution, which contains the greater portion of the ammonium malate, is filtered from the separated ammonium oxalate, ammonium tartrate, and ammonium citrate, the malate ion precipitated with lead acetate, and the lead malate washed with 90 per cent. alcohol and submitted to further tests (Barfoed).

If a *little citric acid or malic acid* is to be detected in the presence of *much tartaric acid*, the tartrate ion should first be precipitated with potassium acetate, with the addition of an equal volume of strong alcohol. Citrate or malate ion may be precipitated in the filtrate by means of calcium chloride and ammonia solution if the quantity of alcohol is slightly increased. Finally, the calcium malate may be separated from the citrate by treatment with boiling lime water.[3]

SECOND GROUP OF ORGANIC ACIDS.

The normal calcium salts of the acids of the second group are comparatively readily soluble in water. The solutions of the normal alkali salts give precipitates or colour reactions with ferric chloride solution: *Benzoic acid, salicylic acid, formic acid, acetic acid* (*propionic acid, n-butyric acid, lactic acid*).

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[1] See the illustrations in Behrens, Vol. 4, p. 49.

[2] *Zeitsch. anal. Chem.*, **46**, 261.

[3] With regard to the separation of the acids dealt with here from one another and from several others, *cf.* also W. Keim, *Zeitsch. anal. Chem.*, **30**, 405; C. Micko, *Ibid.*, **31**, 465; N. Schoorl, *Zeitsch. angew. Chem.*, **13**, 367; G. Jorgensen, *Zeitsch. Unters. Nahr. Genuss.*, **17**, 396.

First Division.

The acids of the first division may be sublimed undecomposed. They are only appreciably volatile with steam from their aqueous solutions when strongly concentrated. They are nitrated by nitric acid. They dissolve with difficulty in water, but readily in ether, so that by shaking their aqueous solutions with the latter they are almost completely extracted without difficulty (*benzoic acid*, *salicylic acid*).

Sec. 141.

(a) **Benzoic acid,** $C_6H_5.COOH$ (Benzoate ion, $C_6H_5.CO'_2$).

1. *Benzoic acid* in the pure condition consists of odourless, though generally faintly aromatic, brilliant white flakes or needles, or of a crystalline powder. It melts at 121·4°, and boils at 250°, and volatilises completely. Heated in an open dish, it evaporates to a considerable extent even at 100°. Its vapours have a characteristic irritating effect on the throat, causing coughing. When carefully cooled, they condense as lustrous needles. When ignited they burn with a luminous, smoky flame. The ordinary medicinal benzoic acid has the odour of gum benzoin, and when heated in a test-tube leaves a slightly brown residue. Benzoic acid dissolves at 0° in 588, at 20° in 345, at 100° in 17 parts of water (Bourgoin); it is readily dissolved by alcohol and by ether. A saturated alcoholic solution is, therefore, rendered slightly turbid by water. It may be almost completely extracted from its aqueous solution, or from solutions of its salts strongly acidified with sulphuric acid, by shaking them with ether. It is a weak acid (dissociation constant 6.10^{-1}); its aqueous solutions are, therefore, only dissociated to a slight extent; they have an acid reaction. It dissolves to a colourless liquid in concentrated sulphuric acid, from which it is precipitated by water unchanged. It is volatile in steam; it may be expelled almost completely in a current of steam from its concentrated aqueous solutions, or from the concentrated solutions of its salts strongly acidified with sulphuric acid. Benzoic acid remains unchanged when heated with an alkaline solution of potassium permanganate. When treated with strong nitric acid it is converted into nitro-benzoic acid.

2. *Benzoic acid salts* (*benzoates*) are mainly soluble in water; only those are practically insoluble which contain weak cations. Soluble benzoates have a characteristic, irritating taste; they are

dissociated in aqueous solution to a normal extent. If a strong *acid* is added to concentrated aqueous solutions of benzoates, the benzoate ions combine with hydrogen ions to form benzoic acid, which separates in the form of a dazzlingly white, crystalline powder, dissolving with difficulty. In the same way benzoic acid is precipitated from its insoluble salts on the addition of strong acids, which form soluble salts with the cations with which the benzoate ion was combined.

3. **Ferric chloride solution**, prepared in the cold (Sec. 138, 5) precipitates benzoate ion almost completely from solutions of benzoates. The precipitate consists mainly of the *benzoate* of the *hexabenzoatotriferric* base,[1] $C_6H_5.COO[(OH)_2\overset{III}{Fe}_3(C_6H_5\,COO)_6]$. The voluminous flesh-coloured precipitate is decomposed on treatment with ammonia solution in a similar manner to basic ferric succinate, but differs from the latter in that it dissolves in a small quantity of hydrochloric acid, with the separation of the greater portion of the benzoic acid. Alkali tartrates prevent or influence the precipitation of the ferric compound.

4. *Lead acetate solution* does not precipitate free benzoic acid, but precipitates benzoate ion in a flocculent form. The precipitate $(C_6H_5.COO)_2Pb+H_2O$ does not dissolve in the presence of an excess of benzoate ion, but it is soluble in an excess of lead acetate solution, as also in acetic acid. When the solution containing the precipitate is heated to boiling point, the latter is not dissolved, even on the addition of ammonia solution

5. On treating a solution of benzoic acid or of a benzoate with *barium or* **calcium chloride solution,** ammonia solution, and dilute alcohol, *no precipitate* is formed. (Distinction from succinic acid.)

6. *Silver nitrate solution* does not produce a precipitate in solutions of free benzoic acid, but on the addition of sodium acetate crystalline *silver benzoate* is precipitated, $C_6H_5\,COOAg$ It forms a white precipitate in solutions of benzoates on the addition of silver nitrate solution. Silver benzoate is readily soluble in ammonia solution, as also in a large quantity of boiling water

7. Benzoic acid is esterified by a single boiling with a little absolute **alcohol and concentrated sulphuric acid.** If, when cool, the test-tube is filled nearly to the top with water and 5 c.c. of ether, and then shaken, the *benzoic acid ethyl ester*, $C_6H_5\,COO(C_2H_5)$, is taken up by the ether. On dipping a strip of filter paper into

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[1] R. F. Weinland and A. Herz, *Ber.*, **45**, 2662.

the latter, the ester may be recognised on it, after evaporation, by its odour (A. Röhrig[1]).

8. On evaporating an alkaline solution containing benzoate ion to about 0·5 to 1 c.c., *acidifying* it on a clock glass, adding a granule of **sodium amalgam,** then covering it with another clock glass, the strong odour of *benzaldehyde*, $C_6H_5.CHO$ (recalling that of bitter almonds), will become noticeable when the glasses are opened, after the evolution of hydrogen has ceased (K. B. Lehmann[2]).

9. If a small quantity of a slightly alkaline solution of benzoic acid or of a soluble benzoate is evaporated to dryness in a test-tube on a suitable bath heated to 110°–115°, the residue cooled and then slowly heated with a small quantity of a mixture of 2 parts of *concentrated sulphuric acid* and 1 part of *concentrated nitric acid* in an oil bath (a small beaker with paraffin oil) to 240°, 1 c.c. of water carefully added when the mixture is cool and the latter treated when again cool with an excess of *ammonia solution*, a *yellow coloration* will generally appear. On boiling the mixture, cooling it, and dropping on to it a 10 per cent. *sodium monosulphide solution* (freshly prepared by dissolving crystallised sodium sulphide in cold water), a *reddish-brown* ring will appear almost immediately, the colour of which is imparted to the whole liquid when shaken. On boiling the mixture the former yellow coloration returns. In this reaction there is first formed (owing to the action of the acid mixture) dinitrobenzoic acid, which is then further reduced by the sulphide to nitro-*m*-aminobenzoic acid, $C_6H_5.\overset{1}{N}O_2.\overset{3}{N}H_2.C\overset{5}{O}OH$, and to *diaminobenzoic acid*, $C_6H_3.\overset{1}{N}H_2.\overset{3}{N}H_2C\overset{5}{O}OH$, the ion of which dissolves, showing a reddish-brown colour (E. Mohler,[3] C. von der Heide and F. Jakob[4]).

10. Benzoic acid is oxidised by **hydrogen peroxide** to *salicylic acid*. On boiling 4 c.c. of an aqueous benzoic acid solution with 0·2 c.c. of acetic acid, 0·2 c.c. of ferric chloride solution, and 0·2 c.c. of hydrogen peroxide solution by placing it in a boiling water bath, there will appear after 10 or 15 seconds the characteristic *violet* coloration due to the resulting salicylic acid (Jonescu, Denigès[5]). (Distinction from cinnamic acid.)

The sensitiveness of the reaction depends on the ratio of hydrogen peroxide to benzoic acid; mineral acids, volatile fatty acids, and other volatile acids, and also alcohol, have a preventive action (O. Biernath [4]).

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[1] *Zeitsch. anal. Chem.*, **53,** 455.

[2] *Ibid*, **53, 461.**

[3] *Ibid.*, **36,** 202.

[4] *Ibid.*, **53, 459.**

[5] *Ibid.*, **51,** 686.

11. Benzoic acid is partially converted into *salicylic acid* also by *fusion with alkali* under certain very limited conditions. Benzoic acid is dissolved in a few drops of sodium hydroxide solution and about 1 c.c. of water, evaporated to dryness in a silver crucible on the water bath, and then fused over a small flame with 2 grms. of coarsely pulverised potassium hydroxide and kept in a state of fusion for 2 minutes, while being stirred with a thick platinum wire. On dissolving the fused mass in water, acidifying the solution with sulphuric acid, shaking it with ether, and evaporating the ether solution (previously washed three times by shaking it with a little water) with 1 c.c. of water at a low temperature, the aqueous residue will give with ferric chloride solution the *violet colour reaction* of salicylic acid (K. Fisher and O. Gruenert [2]).

12. With regard to the *microchemical detection* of benzoic acid, see Haushofer, p. 71 and Behrens, Vol. 4, p. 71.

SEC. 142.

(b) **Salicylic acid** (Ortho-hydroxybenzoic acid), $C_6H_4.(\overset{1}{OH}).(\overset{2}{COOH})$ (Salicylate ion, $C_6H_4(OH).COO'$).

1. *Salicylic acid* is a fairly weak acid (dissociation constant 1.10^{-3}), and only undergoes slight dissociation in its aqueous solution. It crystallises in the form of colourless and odourless needles or rods. It dissolves slightly in cold and more readily in hot water, one part requiring 666 parts of water at 0°, 370 parts at 20°, and 12·6 parts at 100° (Bourgoin). It is exceedingly soluble in alcohol and in ether, as also in amyl alcohol and chloroform. From its aqueous solutions or acidified solutions of its salts, it may be almost completely extracted by shaking with ether or chloroform. Salicylic acid melts at 155°, and when carefully heated sublimes unchanged in the form of needles; when rapidly heated it is partly decomposed into carbon dioxide and phenol. When an aqueous salicylic acid solution is boiled, it volatilises to a considerable degree, and may to a large extent be expelled from its strongly concentrated aqueous solutions or from solutions of its salts, acidified with sulphuric acid, by continuous distillation in a current of steam. Its aqueous solutions give a distinctly acid reaction. The action of strong nitric acid on hot salicylic acid produces nitrosalicylic acids. It is completely

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[1] *Zeitsch. anal. Chem.*, **53**, 462.

[2] *Ibid.*, **53**, 456.

decomposed when heated with an alkaline solution of potassium permanganate.

2. Salicylic acid forms with bases *two series of salts* (salicylates), which are generally termed neutral and basic. In the "neutral" salts only the hydrogen of the carboxyl group is replaced, and in the "basic" salts that of the hydroxyl group as well. The aqueous solutions of salicylates are dissociated to a normal extent, those of the basic salts being also considerably hydrolysed, so that they give an alkaline reaction. Solutions of the alkali salts turn brown when heated in the air, especially if they contain basic salts. Most of the neutral salicylates are soluble in water, but of the basic salicylates many do not dissolve in water or only slightly. The alkali salts of salicylic acid are converted when heated at definite high temperatures into salts of *p*-hydroxybenzoic acid. When heated with an excess of alkali either a conversion into *p*-hydroxybenzoates will occur, or partial decomposition, with the formation of carbon dioxide and phenol, or the salts remain unchanged, according to the temperature and the quantity of the excess of alkali (H. Ost[1]). The salts of the alkaline earths and heavy metals are partly decomposed at temperatures between 200° and 400° into carbon dioxide and phenol; conversion into *p*-hydroxybenzoate does not take place (A. v. d. Velden[2]). *Mineral acids* precipitate *salicylic acid* from sufficiently concentrated solutions of salicylates as a *crystalline white precipitate*. Acetic acid does not cause precipitation

3. *Lead acetate solution* produces in the solutions of neutral alkali salicylates a white precipitate of lead salicylate, $(C_6H_4OH COO)_2Pb+H_2O$, which dissolves in excess of lead acetate as also in acetic acid, but not in ammonia solution. The precipitate dissolves if the solution is heated; it separates in small crystals when the solution cools.

4. **Calcium chloride,** as also *barium chloride*, does not yield precipitates in solutions of alkali salicylates, even on the addition of ammonia solution and dilute alcohol.

5. *Silver nitrate solution* produces in a solution of sodium salicylate a voluminous white precipitate of *silver salicylate*, $C_6H_4 OH.COOAg$, which becomes crystalline on standing. It is readily soluble in ammonia solution.

6. On mixing a solution of salicylic acid in **methyl alcohol** with half its volume of **concentrated sulphuric acid,** and heating it,

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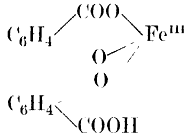
[1] *J. prakt. Chem.*, N. F., **11**, 392.

[2] *Ibid.*, N. F., **15**, 160.

a compound, the methyl ester of salicylic acid, with an aromatic odour, is formed, and may be separated by distillation; this is the chief ingredient of oil of wintergreen. By dissolving salicylic acid in ethyl alcohol, the corresponding ethyl compound, with a similar odour, is formed after the solution has been allowed to stand in a warm place.

7. On adding to an aqueous solution of not appreciably dissociated salicylic acid a small quantity of freshly prepared **ferric chloride solution,** more or less dilute according to the quantity of salicylic acid, the liquid will assume an *intense violet coloration.* Free formic acid, acetic acid, butyric acid, lactic acid, tartaric acid, citric acid, and other hydroxy acids influence the sensitiveness of this very characteristic reaction; hydrochloric acid and ammonia prevent it. The reaction is based on the formation of *ferric salts of disalicylatoferric acid:*



The solution of a salicylic acid salt reacts at first somewhat differently from the free acid. On adding very dilute ferric chloride solution, drop by drop, to a concentrated solution of sodium salicylate, there will be formed first a fiery reddish-yellow and then, on further addition, a red coloration (similar to that of ferric thiocyanate), and only on a still further addition the violet reaction, which is also shown by the free acid. The reddish-yellow coloration depends on the formation of *trisalicylatoferric acid*, $\overset{III}{Fe}(O.C_6H_4.COOH)_3$, the red coloration on the formation of disalicylatoferric acid, and the violet on the formation of the above-mentioned ferric salts of the latter (R. F. Weinland and A. Herz[1]). A **considerable** excess of ferric chloride causes the violet colour to change into red tinged with brown in the case of both salicylic acid and salicylates.

8. On boiling an aqueous salicylic acid solution with a few drops of a 10 per cent. **mercuric nitrate solution** (prepared by heating 10 grms. of mercuric nitrate with 90 c.c. of water until nearly boiling, adding concentrated nitric acid drop by drop until, while stirring the mixture and pressing the solid particles with a glass rod, all the basic salt is dissolved, and finally adding water

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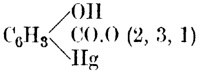
[1] *Liebig's Ann. d. Chem.*, **400**, 219.

up to 100 c.c.), adding two or three drops of *dilute sulphuric acid*—if necessary boiling the mixture—and finally drop by drop 1 per cent. *sodium nitrite solution*, a *red coloration* will appear, which generally becomes more marked on cooling (Millon's reaction). This reaction is based on the fact that first a complex *mercuric salicylic acid* is formed:



$$C_6H_3\begin{cases}OH \\ CO.O \\ Hg\end{cases} (2, 3, 1)$$

which then yields with nitrite ion a nitroso compound, which dissolves in the presence of mercuric nitrate, forming a red solution (C. J. Lintner[1]). All other substances which contain the hydroxyphenyl group [$C_6H_4(OH)\_$], including the proteins, show in this test a red coloration which is due to a corresponding mechanism of reaction.

9. On heating 10 c.c. of a salicylic acid solution with 4 drops of a 10 per cent. *potassium or sodium nitrite solution*, 4 drops of *acetic acid*, and 1 drop of 10 per cent. *cupric sulphate solution* for some time in a boiling water bath, a *blood-red coloration* is produced (A. Jorissen[2]).

10. Although when Mohler's reaction, described in connection with benzoic acid (Sec. 141, 9), is used, salicylate ion gives a bright yellow coloration when neutralised with ammonia solution, the formation of the reddish-brown zone when sodium monosulphide solution is poured on to the mixture does not occur, or occurs at most after a few minutes. If, on the other hand, the solution is then boiled a very deep reddish-brown coloration appears—a further contrast to the behaviour of benzoate ion. If the monosulphide solution is replaced by a sodium polysulphide solution or by yellow ammonium sulphide, the red-brown zone appears immediately, even in the cold.

11. Salicylic acid is almost completely precipitated from its aqueous solution by *bromine water* as symmetrical *tribromophenol*, $C_6H_2Br_3.OH$ (2, 4, 6, 1), in the form of white flakes; on the addition of a sufficient excess of bromine this is converted into yellowish-white almost insoluble *p*-ketodihydrotetrabromobenzene, $CO<\genfrac{}{}{0pt}{}{CBr=CBr}{CBr=CBr}>CH_2$ (R. Benedikt[3]).

12. With regard to the *microchemical detection* of salicylic acid, see Behrens, Vol. 4, p. 80.

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[1] *Zeitsch. angew. Chem.*, **13**, 707.

[2] *Zeitsch. anal. Chem.*, **42**, 458.

[3] *Liebig's Ann. d. Chem.*, **199**, 135.

SECOND DIVISION

Of the second group of organic acids.

The acids of the second division dissolve very readily in water. With the exception of lactic acid they volatilise readily with steam, and may be almost completely expelled without difficulty from fairly dilute solutions: *Formic acid, acetic acid* (*propionic acid, n-butyric acid, lactic acid*).

SEC. 143.

(a) **Formic acid,** $H.COOH$ (Formate ion, $H.COO'$).

1. *Formic acid* is a colourless, transparent, corrosive, slightly fuming liquid, with a very penetrating and characteristic odour. It crystallises at − 1° in colourless leaves, which melt at +8·3°. It is miscible with water and alcohol in all proportions. It boils at 101°, and can be distilled without decomposition. Its vapours can be ignited and burn with a blue flame. When distilled in a current of steam it may be completely expelled without difficulty, even from only slightly concentrated solutions.

It is a weak acid (dissociation constant $1.14.10^{-4}$ at 25°), and therefore only slightly dissociated in its aqueous solutions. It is readily and completely oxidised when heated with chromic acid, or with potassium permanganate in alkaline solution.

2. Nearly all the *formic acid salts* (*formates*) are fairly readily soluble in water, the greater number dissolve with difficulty in alcohol. They are dissociated to a normal extent in aqueous solution, and at this stage are not hydrolysed to any appreciable degree. The solutions of the alkali salts, therefore, show a neutral reaction towards litmus. When heated to a fairly high temperature (the sodium salt at about 290° to 360°) the alkali salts, especially in the presence of a free alkali, are converted almost completely into oxalates with the liberation of hydrogen:

$$2H.COONa = H_2 + (COO)_2Na_2$$

When ignited, the formates give a residue of carbonates, oxides, or metals; carbon separates simultaneously, and inflammable gases, carbon dioxide, and water escape.

3. On adding **ferric chloride** to a dilute formic acid solution and almost neutralising it with ammonia, or on mixing the neutralised solution of a formate with ferric chloride solution, the liquid will assume a *dark red* colour (provided the ferric chloride

remains in excess). When boiled it becomes colourless (if too much ferric chloride was not added), since all the iron separates in brownish-yellow flakes mainly as *basic ferric formate*. The red coloration of the solution depends mainly on the formation of the cation of the *hexaformatotriferric base* $[(H.COO)_6\overset{III}{Fe}_3]^{\cdots}$. In the presence of very much sodium formate with little ferric chloride, *e.g.* on the addition of a small quantity of the latter to a saturated solution of the former, a light green coloration is first produced, owing to the formation of the anion of the *hexaformatomonoferric base* $[(H.COO)_6\overset{III}{Fe}]'''$, which is only replaced by the red coloration on a considerable addition of ferric chloride (R. F. Weinland and H. Reihlen [1]). The red coloration changes to yellow on the addition of hydrochloric acid (Distinction from thiocyanate ion.) Ammonia precipitates all the iron from the red solution as ferric hydroxide.

4. **Silver nitrate** does not precipitate free formic acid, and only precipitates alkali formates in concentrated solutions. The crystalline, white, sparingly soluble precipitate of *silver formate*, $H.COOAg$, soon becomes darker through the separation of metallic silver. On standing for some time complete reduction takes place, even in the cold, but on heating the liquid with the precipitate it takes place immediately. The same reduction also occurs if the solution of the formate was so dilute that no precipitate was produced, or if free formic acid was present. It does not occur, however, in the presence of ammonia in excess, and it is also prevented by the presence of small quantities of chlorine ion (H. Sultzer [2]) The reaction is based on the fact that two formate ions, while losing their negative charge, are converted into carbon dioxide and formic acid, whereby naturally an equivalent quantity of silver ion must lose its positive charge: $2H.COO'+2Ag^{\cdot}=CO_2+H{\cdot}COOH+2Ag$.

5. **Mercurous nitrite solution** produces no precipitate in free formic acid, but in solutions of alkali formates it yields a glistening white, sparingly soluble precipitate of *mercurous formate*, $(H.COO)_2Hg_2$. Owing to the separated mercury, this precipitate soon becomes grey; complete reduction takes place after long standing, even in the cold, but immediately on heating, whereby carbon dioxide and formic acid are also formed. As in the case of the silver salt, the reduction takes place even when the liquid is so dilute that the mercurous formate remains dissolved, or if free formic acid is present.

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[1] *Ber.*, **46**, 3144.

[2] *Zeitsch. angew. Chem.*, **25**, 1273.

6. On heating an aqueous solution of formic acid or of an alkali formate with several times its quantity of **mercuric chloride,** a precipitate of *mercurous chloride* is obtained:

$$H.COO' + 2Hg^{\cdot\cdot} + 4Cl' = H^{\cdot} + CO_2 + Hg_2Cl_2 + 2Cl'$$

for example—

$$H.COONa + 2HgCl_2 = Hg_2Cl_2 + CO_2 + NaCl + HCl$$

The presence of large quantities of free hydrogen ion, *e.g.* free hydrochloric acid, prevents the reaction; in such cases, however, it takes place on the addition of a corresponding quantity of sodium acetate. Such an addition may also be recommended to check the dissociation of the acid liberated on the reaction.

7. On heating dilute formic acid with an excess of *lead oxide*, the latter will partially dissolve (the liquid will show an alkaline reaction). When the solution, if necessary concentrated by evaporation, is cool, *lead formate*, $(H.COO)_2Pb$, separates in glistening rods or needles, which are practically insoluble in alcohol. (Distinction from acetic acid.)

8. When heated with concentrated *sulphuric acid*, formic acid or a formate decomposes (without a blackening of the liquid) into water and carbon monoxide which escapes with effervescence, and when ignited burns with a blue flame. The sulphuric acid effects the complete decomposition of formic acid: $H.COOH = H_2O + CO$.

On heating formates in a distillation apparatus with dilute sulphuric acid, free formic acid is obtained in the distillate, and may generally be recognised immediately by its odour; on heating it with a mixture of concentrated sulphuric acid and alcohol, the ethyl ester of formic acid is produced, which may be recognised by its characteristic odour, reminiscent of that of brandy.

9. On gradually treating a very dilute solution of formic acid or of a formate (previously treated with half its volume of hydrochloric acid) in a small covered flask with a few degrms. of **magnesium turnings,** the formic acid is reduced to *formaldehyde* (H. J. H. Fenton and H. A. Sisson [1]). The latter may be identified by boiling rapidly for a minute 5 c.c. of the clear liquid, decanted after two hours' action, in a good-sized test-tube with 2 c.c. of milk and 7 c.c. of hydrochloric acid of sp. gr. 1·12, to every 100 c.c. of which 0·2 c.c. of a 10 per cent. ferric chloride solution has been added. In the presence of formaldehyde a *violet coloration* will appear. A preliminary test should be made to determine whether on the one

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[1] *Chem. Zentr.*, 1908, I., p. 1379.

hand the milk is free from formaldehyde and, on the other, whether it will show the reaction on the addition of a very small quantity of formaldehyde. Large quantities of formaldehyde influence or prevent the colour reaction.

10. With regard to the *microchemical detection* of formic acid, see Haushofer, p. 68; Behrens, Vol. 4, p. 21.

SEC. 144.

(b) Acetic acid, $CH_3.COOH$ (Acetate ion, CH_3COO').

1. *Acetic acid* is known in the form of transparent, flaky crystals, which melt at +16·6° to a colourless liquid with a characteristic penetrating odour and a very acid taste (*glacial acetic acid*). This boils at 118·1° and volatilises in the form of inflammable vapours, which burn with a blue flame and emit a penetrating odour. Acetic acid is miscible with water in all proportions. Such mixtures are inaptly called acetic acid. Acetic acid is a very weak acid (dissociation constant $1{\cdot}8.10^{-5}$ at 25°); its aqueous solutions only undergo slight hydrolysis. It may be completely expelled from dilute aqueous solutions without difficulty by means of distillation in a current of steam. Acetic acid also dissolves in alcohol. It is fairly stable towards potassium permanganate both in acid and in alkaline solution.

2. *Acetic acid salts* (*acetates*) are decomposed on ignition. The alkali salts and other salts with strongly positive metal ions yield mainly acetone, $CH_3.CO.CH_3$, and carbon dioxide, which, according to the nature of the metal ions, combines with them to form carbonates, or escapes. In the case of salts with weakly basic metal ions a large portion of the acetic acid escapes undecomposed. The residues mainly contain carbon. Nearly all the acetates are soluble in water and dilute alcohol; most of them dissolve readily in water, and only a few dissolve with difficulty. The acetates are dissociated to a normal extent in aqueous solutions; the concentrated solutions of alkali salts are appreciably hydrolised and show an alkaline reaction towards litmus. On heating acetates with dilute sulphuric or phosphoric acid in a distillation apparatus, free acetic acid is obtained in the distillate.

3. On adding **ferric chloride solution** to dilute acetic acid and almost neutralising the acid with ammonia solution, or on mixing the neutralised solution of an acetate with ferric chloride solution, the liquid assumes a very dark red colour, which may be attributed

to the formation of the complex cation of a *hexacetotriferric base*, $[(CH_3.COO)_6\overset{III}{Fe_3}(OH)_2]^{\cdot}$ (R. F. Weinland and E. Gussmann[1]). When boiled the solution becomes colourless if acetate is present in excess, whilst all the iron, whether in the form of other complex salts or as a basic ferric acetate, is precipitated in brownish-yellow flakes. Ammonia solution precipitates all the iron from the red solution as *hydroxide* ; the red liquid becomes yellow on the addition of hydrochloric acid. (Distinction from thiocyanogen ion.)

4. Solutions of neutral acetates, but not free somewhat dilute acetic acid, give with *silver nitrate solution* a crystalline white precipitate of *silver acetate*, $CH_3\,COOAg$, which dissolves with difficulty in cold water (one part in 97·7 parts of water at 25°).[2]

It dissolves more readily in hot water, and when the solution is cool separates in the form of very fine crystals. Ammonia solution readily dissolves it ; free acetic acid does not increase the solubility in water, but free nitric acid does. The precipitate is not reduced by the method described for silver formate in Sec. 143, 4. (Distinction from formate ion)

5. *Mercurous nitrate solution* produces in acetic acid, especially if dilute, and still more readily in acetate solution, a scaly crystalline white precipitate of *mercurous acetate*, $(CH_3.COO)_2Hg_2$, which dissolves with difficulty in the cold (1 part in 133 parts of water at 12° to 15°), but easily in excess of the precipitant.

It dissolves when heated with water, and when cool is reprecipitated in the form of small crystals. The mercurous acetate, however, is partially decomposed hereby, mercury separates in metallic form and imparts a grey coloration to the precipitate. If dilute acetic acid is used for boiling instead of water, the quantity of metallic mercury which separates is exceedingly small.

6. **Mercuric chloride** when heated with acetic acid or the solution of an acetate does not produce a precipitate of mercurous chloride. (Distinction from formic acid.)

7. If dilute acetic acid is heated with an excess of *lead oxide*, part of it dissolves as basic lead acetate. The liquid shows an alkaline reaction and does not form crystals on cooling.

8. On heating acetates with **concentrated sulphuric acid,** acetic acid is evolved, and may be recognised by its pungent odour. If the salts are heated with a mixture of approximately equal volumes of **concentrated sulphuric acid and alcohol,** the ethyl ester of acetic

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[1] *Zeitsch. anorgan. Chem.*, **66**, 157.

[2] H. Armstrong and J. Vargas Eyre, *Chem. Zentr.*, 1913, I., 1803.

acid is evolved, $CH_3.COO(C_2H_5)$; its characteristic pleasant odour is particularly noticeable when the slightly cooled mixture is shaken, and consequently scarcely permits of an error, or at least less seldom than does the pungent odour of the free acid.

9. Solid alkali acetates, when heated with about an equal quantity of **arsenic trioxide** in a test-tube, yield a very poisonous gas with an exceptionally characteristic repulsive odour, *cacodyl oxide* (alkarsine, dimethylarsenic oxide) :

$$4CH_3.COOK+As_2O_3 \quad [(CH_3)_2As]_2O+2K_2CO_3+2CO_2$$

The reaction is very sensitive and for the sake of safety should be carried out with small quantities.

10. With regard to the *microchemical detection* of acetic acid, see Haushofer, p. 76 ; Behrens, Vol. 4, p. 24.

Sec. 145.

Summary and Remarks.

1. A general test for the acids of the second group is made by adding ferric chloride solution to the aqueous solution which has been rendered neutral towards litmus. If *only one* organic acid or its anion is presumed to be present, the result of the reaction enables conclusions to be drawn at once as to the nature of the acid. A flesh-coloured precipitate indicates benzoic acid, a violet coloration salicylic acid, and a reddish-brown coloration formic or acetic acid, which may be distinguished from one another by their behaviour towards mercuric chloride (Sec. 143, 6) or their behaviour when boiled with sulphuric acid and alcohol (Sec. 144, 8). It should, of course, be noted that the organic acids of the second subdivision of the first group, as also thiocyanogen ion, also show a reaction with ferric chloride ; the absence of the former must, therefore, if necessary be determined by their behaviour towards calcium chloride. The absence of thiocyanogen ion may be determined by the fact that the reaction disappears on the addition of hydrochloric acid.

2. If *several* acids of the second group as well as those of the first group are to be taken into consideration, the following course may be recommended. (*a*) The formic acid and the acetic acid are first expelled by distillation in a current of steam from the solution [1]

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[1] If during acidification any cinnamic, benzoic, or salicylic acid is precipitated (*cf.* Sec. 139, 2, p. 514), it should be removed by means of filtration before distillation to prevent its being carried over with the steam. The ethereal solution of the separated portion should then be added to the ethereal extract of the distillation residue subsequently obtained.

(sufficiently acidified with sulphuric acid and so dilute that any salicylic or benzoic acid present is not expelled in any considerable quantity), and benzoic acid and salicylic acid then extracted from the distillation residue by shaking it once with an equal volume of ether. In this way any cinnamic acid present is dissolved by the ether, and must therefore be taken into consideration in the further course of the examination.

(*b*) The distillate obtained may contain, in addition to formic and acetic acids, still higher fatty acids (*cf.* Secs. 146 and 147), and also volatile mineral acids (hydrochloric acid, nitric acid), if the corresponding anions were present in the original material. Sulphate ion may also be reduced to sulphur dioxide by many organic substances in the course of the distillation, and will then be present in the distillate as sulphurous acid. To avoid this, phosphoric acid solution may be used in such cases instead of sulphuric acid for acidification prior to the distillation.

The distillate is treated with pure sodium carbonate in excess, strongly concentrated (when disturbing volatile substances such as aldehyde, etc., will escape), and then submitted to further tests. When distilling with steam, instead of introducing the steam charged with the volatile substances directly into the condenser, it may be allowed to pass through a flask containing calcium carbonate suspended in water, and finally the liquid containing the calcium formate and calcium acetate is filtered from the excess of carbonate (H. Fincke [1]). (*a*) The final detection of formic acid is effected by testing the behaviour of the solution, obtained by either method, towards mercuric chloride or by reduction to formaldehyde (Sec. 143, 6 and 9). Sulphurous acid or salicylic acid may have a disturbing influence in the first process, the former because it also reduces mercuric chloride, and the latter because with mercuric chloride it gives a precipitate of mercuric-salicylic acid (Sec. 142, 8). The latter difficulty may be overcome by adding sodium chloride before the reduction, as this retains the mercuric-salicylic acid in solution; the former by allowing the concentrated neutralised distillate or the filtrate from the calcium carbonate to stand for about 4 hours, at the ordinary temperature (before starting the reduction test), with about 1 per cent. sodium hydroxide solution and a few c.c. of 3 per cent. hydrogen peroxide; precipitated mercuric oxide stirred up with water is then added to destroy the excess of hydrogen peroxide, and, after half an hour, the liquid is filtered (H. Fincke [1]). (β) The detection of acetic acid in the residue from the evaporation of the neutralised distillate is effected as in Sec. 144, 8. If acetic acid is to be detected in the presence of formic acid, it is advisable to eliminate the latter beforehand by oxidation with chromic acid, whereby water and carbon dioxide are formed, whilst the acetic acid is not attacked. The not too concentrated neutral solution is boiled for 10 minutes beneath a reflux condenser with 1·5 times its volume of a solution of 12 grms. of potassium dichromate in 30 c.c. of concentrated sulphuric acid and 100 c.c. of water, then re-distilled in a current of steam, and the distillate tested for acetic acid (D. S. McNair,[2] F. Schwarz, and O. Weber [3]).

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[1] *Zeitsch. Unters. Nahr. Genuss.*, **21**, 1; **25**, 386.

(γ) The detection of formic acid in substances *containing sugar* cannot be carried out by the method described, since, in the course of distillation in the presence of acid, formic acid is formed from the sugar (Malaguti [4]) and will consequently be found in the distillate, even if it was not originally a constituent of the substance under examination. For the purpose of testing for formic acid, liquids containing sugar should be acidified with sulphuric acid and shaken twice with an equal volume of ether, which will dissolve, if not all, at least a considerable quantity of the formic acid and acetic acid. The combined filtered ethereal extracts are shaken with alkaline water, the latter acidified with sulphuric acid and distilled in a current of steam, and the distillate tested for formic acid and acetic acid (W. Fresenius and L. Grünhut). The distillation residue will contain the acids of the first sub-group, as also cinnamic acid.

(*b*) *The ethereal extract of the distillation residue*, obtained by the methods described above, will contain any benzoic acid, salicylic acid, and cinnamic acid, and these may be separated from it by means of careful evaporation, either in the form of a solid substance or as an aqueous solution by adding water prior to the evaporation. The following reactions may serve for the *final identification* of the isolated acids: Mohler's reaction for benzoic acid (Sec. 141, 9), the colour reaction with ferric chloride for salicylic acid (Sec. 142, 7), and precipitation with solutions of manganous salts and oxidation to benzaldehyde for cinnamic acid (Sec. 139, 3, 7). These reactions, however, are not easy to recognise when several of the acids mentioned are present simultaneously. Benzoic acid can only be recognised unmistakably in the presence of salicylic acid, and cinnamic acid by means of reduction to benzaldehyde (Sec. 141, 8); in the presence of cinnamic acid, but in the absence of salicylic acid, the most trustworthy reaction for benzoic acid is that of Jonescu (Sec. 141, 10).[1] The best method of detecting salicylic acid in the presence of cinnamic acid and benzoic acid is Millon's reaction (Sec 142, 8).

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[1] *Zeitsch. Unters. Nahr. Genuss.*, **21**, 14. See also *Ibid.*, **22**, 94, where Fincke gives a survey of the behaviour of numerous other organic acids towards mercuric chloride.

[2] *Zeitsch. anal. Chem.*, **27**, 398.

[3] *Zeitsch. Unters. Nahr. Genuss.*, **17**, 194.

[4] *Liebig's Ann. d. Chem.*, **17**, 59.

The great resistance of benzoic acid towards the oxidising action of potassium permanganate may be utilised with advantage for the detection of this acid in the presence of salicylic acid, and after the salicylic acid has been destroyed by oxidation, the benzoic acid may be isolated by means of sublimation and then identified. Further directions for this test have been given by E. Polenske.[2] It should be noted that any cinnamic acid present will be oxidised to benzoic acid under the conditions of this test, and will then be found in that form.

The reaction for the detection of salicylic acid by means of ferric chloride is influenced by the presence of numerous organic acids, especially hydroxy acids (Sec. 142, 7); even the small quantities of lactic, tartaric, and citric acids which, when the liquid is shaken with ether, are extracted from it, produce under certain conditions a yellow colour reaction instead of the violet one which was anticipated (O. Langkopf,[3] F. Garni [4]). In all cases in which the presence of the acids mentioned has to be taken into consideration, a mixture of equal parts of ether and petroleum spirit of low boiling point [5] should be used, instead of ether, as an extraction solvent for the detection of salicylic acid. In the analysis of wine, the disturbing influence of tannin is obviated by this method, since it would be extracted to a considerable extent by ether, and then would give green to black colorations with ferric chloride solutions. If, however, in the analysis of wine a blackish, bluish-green, or dirty green colour should still appear in testing the extraction residue with ferric chloride solution, the liquid should be treated with a few drops of sulphuric acid, diluted with water, and again extracted by shaking with a mixture of ether and petroleum spirit.

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[1] C. von der Heide and J. Jacob, *Zeitsch. anal. Chem.*, **53**, 460. With regard to further processes for the separation of benzoic and cinnamic acids, see A. W. K. de Jong, *Chem. Zentr.*, 1910, I, 479; for the separation of benzoic and salicylic acids, J. Schaap, *Zeitsch. anal. Chem.*, **32**, 107.

[2] *Zeitsch. anal. Chem.*, **52**, 390.

[3] *Ibid.*, **42**, 457.

[4] *Ibid.*, **47**, 780.

[5] D. Vitali, *Zeitsch. anal. Chem.*, **47**, 781, recommends the use of toluene for the same purpose.

The so-called maltol,[1] a substance which is found in black malt, occasionally also in beer worts and in beer, behaves towards ferric chloride solution in the same way as salicylic acid, and dissolves simultaneously in the last-mentioned extraction solvent. When the presence of maltol is to be taken into account, the reactions of Millon and of Jorissen should be used as distinctive tests for the identification of salicylic acid (Sec. 142, 8 and 9).

(*c*) If the examination extends not only to the acids of the second group already dealt with, but also to *propionic, butyric*, and *lactic acids*, the two first should be looked for in the distillate containing formic and acetic acid, according to the directions given in Secs. 146 and 147. Lactic acid, on the other hand, will be found almost quantitatively in the distillation residue shaken with ether. This residue is shaken a second time (this time, however, with only half the volume of ether) in order to remove any further traces of cinnamic acid or of the acids of the first division. If the liquid which has thus been shaken is subjected to *continuous extraction* with ether for some hours in a suitable apparatus, lactic acid is obtained. If succinic acid and oxalic acid are present, they mix with the lactic acid: if the extraction is continued too long, malic acid, and finally even citric and tartaric acids, pass into the ether extract.[2] The extract should then be tested for lactic acid as described in Sec. 149

(*d*) If the analytical examination is to be extended to *all the organic acids of the first and second groups*, the anions of the first group may first be precipitated from the solution under examination in the presence of ammonium chloride and ammonia by means of calcium chloride solution *with the addition of alcohol*, and the precipitate then tested as in Sec. 140. If the main quantity of cinnamic acid has not previously been precipitated with hydrochloric acid considerable portions of the cinnamylate ion remain in solution, owing to the solubility of calcium cinnamylate in alcohol, and must be taken into consideration in connection with the acids of the second group. The filtrate from the precipitated calcium salts is tested for these acids (after being evaporated on the water bath) according to the details given in this section. As a rule, however, it is more convenient to test *separate* portions of the mixture under examination according to Sec. 140 for the acids of the first group, and according to this section for the acids of the second group. See also Sec. 176 (181).

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[1] J. Brand, *Zeitsch. anal. Chem.*, **36**, 57; H. C. Sherman and A. Gross, *Ibid.*, **52**, 121.

[2] N. Schoorl, *Zeitsch. angew. Chem.*, **13**, 367.

MEMBERS OF RARER OCCURRENCE OF THE SECOND GROUP OF ORGANIC ACIDS

SEC. 146.

1. **Propionic acid,** $C_2H_5.COOH$ (Propionate ion, $C_2H_5.COO'$).

Propionic acid is formed under very varied conditions, as, for example, in fermented liquids as a fermentation product of certain bacteria. It is a colourless liquid with a penetrating and a strongly acid taste. This liquid is miscible with water in all proportions, solidifies in a freezing mixture, and then melts at −22°. It boils at +140·7°. It is as weak an acid as acetic acid (dissociation constant $1.4.10^{-5}$ at 25°). It may be "salted out" from its aqueous solutions by phosphoric acid or by calcium chloride in the form of an oily layer; it volatilises undecomposed, and may be completely expelled without difficulty in a current of steam, even from its fairly dilute aqueous solutions. It is oxidised by potassium permanganate in acid solution to acetic acid, and in hot alkaline solution to oxalic acid and carbon dioxide (E. Przewalsky [1]). The *propionic acid salts* (*propionates*) are, on the whole, readily soluble in water, especially the *calcium salt*; *silver salt* dissolves with difficulty (1 part in 119 parts of water at 18°). Propionate ion behaves like acetate ion towards *ferric ion*; the propionates give a reaction with *arsenic trioxide* similar to the cacodylic reaction (Sec. 144, 9). For the microchemical detection, see Behrens, Vol. 4, p. 27.

SEC. 147.

2. **Normal Butyric acid** $C_3H_7.COOH$ (*n*-Butyrate ion, $C_3H_7.COO'$).

Normal butyric acid is found in a few fats (cow's butter), and also in animal and vegetable substances, but especially in the fermentation products of certain specific bacteria (butyric acid bacteria). It is a colourless liquid with an unpleasant rancid odour when dilute, and an odour similar to that of acetic acid when pure. It solidifies in flakes at −19°, and melts at −7·9°. It boils at +163·5°. Its strength is similar to that of acetic acid (dissociation constant $1.5.10^{-5}$ at 25°). It is miscible with water, alcohol, and ether in all proportions. Like propionic acid it may be "salted out" from its aqueous solutions by means of calcium chloride as an oily layer; it volatilises undecomposed, and may be completely expelled without difficulty from dilute aqueous solutions in a current of steam. It behaves like propionic acid towards potassium permanganate, except that in its oxidation in alkaline solution propionic acid is formed in addition to oxalic acid (E. Przewalsky). Most of the *normal butyric salts* (*n-butyrates*) are also soluble in water, especially the *calcium salt.* The latter dissolves with more difficulty in hot than in cold water (100 parts of water dissolve 19·8 parts of salt containing water of crystallisation at 15°; 16·5 parts at 60°; and 17·4 parts at 100° (O. Hecht [1]), so that a cold saturated solution becomes turbid on boiling, and clear again when cooled. The silver salt dissolves with difficulty (1 part in 200 parts of water at 14°). Butyrate ion behaves in a similar manner to acetate ion towards *mercurous nitrate* (*or chloride*) *solution* (Sec. 144, 5). On the addition of *ferric chloride solution* to the solution of an alkali butyrate, a yellowish-brown precipitate, which is bright red in the case of concentrated solutions, is formed, its separation being accelerated by heating or shaking. Free butyric acid does not give a precipitate with ferric salts. For the microchemical detection, see Behrens, Vol. 4, p. 28.

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[1] *J. prakt. Chem.*, N. F., **88**, 500.

SEC. 148.

Summary and Remarks on Rarer Organic Acids.

The *certain detection* of these and other higher fatty acids is hardly possible within the limits of the ordinary chemical-analytical methods, especially by means of precipitation reactions, and as a rule further methods have to be borrowed from the technique of organic chemistry. According to E. Duclaux [2] a differentiation in pure aqueous solutions may be based on the relative proportion of the acidity of the individual fractions to one another obtained by fractional distillation. As a method of distinction H. Agulhon [3] makes use of the behaviour of a solution of the sodium salts, treated with cupric sulphate solution, towards various organic extraction agents, *i.e.* the colours which the latter assume.

For the separation of individual fatty acids from one another the processes of fractional distillation, fractional precipitation, and fractional crystallisation, in suitable combination with each other, are usually employed, but frequently the quantitative analysis of the silver salts is used as well. By such methods, for example, Scherer [4] tested the mineral springs at Bad Brückenau, and R. Fresenius [5] the sulphur spring at Weilbach, for the fatty acid anions present in them.

E. Linnemann [6] described the following process for the separation of propionic acid from acetic and formic acid. If a mixture of these three acids is evaporated to dryness with water and excess of lead oxide, cold water will extract from the residue practically only a basic lead propionate, which, on heating the filtered solution, is precipitated in the form of crystals, with the composition $(C_2H_5COO)_6Pb_7O_4$. J. Schütz [1] points out that in such a process under certain conditions the greater portion of the acids must escape during evaporation with lead oxide, owing to hydrolytic dissociation of the lead salts, and consequently be lost.

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[1] *Liebig's Ann. d. Chem.*, **213**, 72.

[2] *Ann. de chim. et phys.*, 5 ser., **2**, 289; *Ann. de l'Institut Pasteur*, **9**, 265. *Cf.* also A. Stein, *J. prakt. Chem.*, N. F., **88**, 83.

[3] *Chem. Zentr.*, 1913, II., 86.

[4] *Liebig's Ann. d. Chem.*, **99**, 262, 267, and 279.

[5] *J. prakt. Chem.*, **70**, 15.

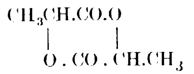
[6] *Liebig's Ann. d. Chem.*, **160**, 223.

SEC. 149.

3. Lactic acid, $CH_3.CH(OH).COOH$ (Lactate ion, $C_2H_4(OH).COO'$).

Lactic acid [2] (*α-hydroxypropionic acid, ethylidine lactic acid*) is known in three stereoisomeric forms: *d*-lactic acid or paralactic acid (*e.g.* as contained in the fluid of the muscular tissue), *l*-lactic acid, and "racemic," inactive (*d*+*l*)-lactic acid. The last is the so-called *ordinary* or *fermentation lactic acid*; it is produced by fermenting sugars with specific bacteria, and is found in sour milk, sauerkraut, sour hay, and in beer. It is present in wine as the product of bacterial decomposition of malic acid. The three forms are distinguished from one another only by their optical behaviour and by the solubility of some of their salts; their reactions are the same. The structurally isomeric *ethylene lactic acid* (*β-hydroxypropionic acid*), $CH_2(OH).CH_2.COOH$, is quite different from them.

Lactic acid is a syrup, which dissolves with difficulty in ether, and is miscible with water and alcohol in any proportion; it does not solidify at 24°, and only boils without decomposition at a very reduced pressure. It volatilises with steam only slightly in dilute solutions, but to a greater extent in solutions concentrated to the consistency of syrup. It is a somewhat stronger acid than succinic acid and acetic acid (dissociation constant $1.34.10^{-4}$ at 25°). It can be extracted only to a comparatively slight degree from its aqueous solutions by shaking with ether, but, on the other hand, may be almost completely expelled without difficulty by means of continuous extraction with ether. When heated at 140°, or when allowed to stand in the cold, and also when kept for some time in aqueous solution, lactic acid changes more or less into *lactic anhydride* (dilactilic acid), $CH_3.CH(OH).COO.CH(CH_3).COOH$, and into *lactide*:



$$\begin{array}{l} CH_3CH.CO.O \\ \quad\;\; | \qquad\quad | \\ \quad\;\; O.CO.CH.CH_3 \end{array}$$

It is, therefore, necessary for the analytical detection of lactic acid in not quite fresh solutions to re-convert these compounds into lactate ion by boiling them with an excess of alkali. In the oxidation of lactic acid with nitric acid, oxalic acid is formed; with chromic acid, acetic acid is obtained;

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[1] *Zeitsch. anal. Chem.*, **39**, 18.

[2] Lactic acid does not really belong to the "rarer" acids in the literal sense of the heading to Sec. 146. It is dealt with here, however, for didactic reasons, owing to the insufficiency of its analytical-chemical characteristics.

with potassium permanganate in acid solution, acetaldehyde; in neutral solution, pyrotartaric acid; and in alkaline solution, oxalic acid.

2. Most of the *lactic acid salts* (*lactates*) are soluble in water to an appreciable extent; only the *basic stannous lactate*, $[CH_3.CH(OH).COOSn]_2O$, is practically insoluble, and on mixing an acid stannous chloride solution with sodium lactate solution is precipitated as a crystalline white powder (H. Engelhardt and R. Maddrell [1]).

3. On treating a solution of 0·4 grm. of phenol in 30 c.c. of water with one drop of ferric chloride solution, and adding a solution containing lactic acid, the fine blue colour of the reagent will change to *yellow* (Uffelmann [2]). The reaction depends possibly on the formation of a coloured hexalactotriferric base (G. Calcagni [3]). Oxalic, tartaric, citric, malic, and formic acids give similar reactions; the reaction is influenced by free hydrochloric acid, phosphoric acid, carbonic acid, fatty acids, and salicylic acid, and is masked by thiocyanogen ion. The reaction becomes more distinct if Uffelmann's amethyst-blue reagent is first shaken with ether. By this means it is decolorised; on the addition of the smallest quantity of lactic acid the yellow coloration appears (H. Futh and G. Lockemann [4]). In this process phenol does not take part in the actual reaction; the yellow coloration is therefore also obtained when lactic acid or lactate solutions are added to a ferric chloride solution freshly diluted until practically colourless (Boas [5]), or when a salicylic acid ferric chloride solution is used instead of the phenol ferric chloride solution (H. Kühl [6]).

4. On heating 5 c.c. of lactic acid (dissolved in 10 c.c. of water) or a corresponding quantity of a lactic acid or lactate solution with 5 c.c. of concentrated sulphuric acid in a small distillation flask, it is decomposed into acetaldehyde and formic acid: $CH_3CH(OH).COOH = CH_3.CHO + H.COOH$.

The former may be detected in the distillate by means of *ammoniacal* silver solution, the latter by mercuric chloride solution (Sec. 143, 6) (T. Gigli). A process depending on the colour reactions of the acetaldehyde formed has been described by G. Denigès.[7]

5. On rendering 5 c.c. of a weak lactic acid or lactate solution strongly alkaline with sodium hydroxide solution of about 10 per cent. strength, boiling it for a few minutes and, after removing the flame, adding 1 to 2 c.c. of a reagent which is prepared by adding 5 grms. of methylamine [8] to the filtered solution of 1 grm. of iodine in 50 c.c. of 1 per cent. potassium iodide solution, a very distinct repulsive odour of isonitrile will soon be produced. The reaction is very sensitive; it depends on the fact that the lactate ion is first converted by iodine into formate ion and iodoform, and

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[1] *Liebig's Ann. d. Chem.*, **63**, 97.

[2] *Pharm. Zentralh.*, **28**, 582.

[3] *Chem. Zentr.*, 1913, II., 1457.

[4] *Ibid.*, 1906, I., 1452.

[5] *Pharm. Zentralh.*, **29**, 323.

[6] *Zeitsch. anal. Chem.*, **50**, 55, 596.

[7] *Ibid.*, 189.

[8] The reagent should be kept in a blue bottle with a ground-in stopper and protected from the light.

then the latter by the methylamine into methylisonitrile (methylcarbylamine):

1. $CH_3.CH(OH).COO' + 4OH' + 3I_2 = 2H.COO' + 3I' + CHI_3 + 3H_2O$
2. $CHI_3 + 3OH' + CH_3.NH_2 = 3I' + CH_3.NC + 3H_2O$.

Many substances which also yield iodoform, and consequently might be confused with lactic acid, can be removed by means of distillation before starting the reaction (A. Ch. Vournasos [1]).

W. Croner and W. Cronheim [2] replace the methylamine in this test by aniline, so that finally instead of methylcarbylamine, phenylcarbylamine, $C_6H_5.NC$, which has an equally repulsive odour, is formed.

6. With regard to the microchemical detection, *cf.* Behrens, Vol. 4, p. 45.

7. The analytical detection of lactic acid is rendered considerably more difficult by the fact that not one of the reactions mentioned is really specific. To detect lactic acid with certainty, it must always be isolated as an individual *substance* and identified by *quantitative* methods. Such a procedure is, however, of course only possible if the quantities of lactic acid in question are not too small. The separation is best based on the special degree of its solubility in ether, and on the fact that barium lactate, in contrast for instance to barium succinate and barium oxalate, is soluble in strong alcohol; the identification is then based on the properties of the *zinc salt.* The solution to be tested for lactic acid should therefore, first be acidified with sulphuric acid and any readily volatile acids present distilled from it in a current of steam, the readily soluble acids in it then shaken with a comparatively small quantity of ether, and finally the lactic acid extracted by ether. The ethereal extract obtained is evaporated in the presence of water with repeated shaking at a gentle heat, and the residual aqueous solution neutralised by means of barium hydroxide. Any excess of barium ion is precipitated by the introduction of carbon dioxide into the boiling liquid. The solution of barium salts is concentrated and treated with three times its volume of strong alcohol (separation from oxalic acid and succinic acid). The liquid is filtered, the alcohol evaporated from the filtrate, the residual barium lactate decomposed with sulphuric acid, and the extraction with ether repeated. The extract is again evaporated with water. Under certain conditions the process may be simplified; for instance, it may be possible to begin with the preparation of the barium salt, or, on the other hand, the first extraction may suffice. The solution containing the lactic acid finally obtained is boiled with zinc carbonate beneath a reflux condenser and the zinc lactate obtained by crystallisation, and then quantitatively analysed. The properties of the zinc salt afford a means of *distinguishing between fermentation lactic acid and para-lactic acid* (*d*-lactic acid). The zinc salt of the fermentation lactic acid crystallises with three molecules of water of crystallisation, $(C_3H_5O_3)_2Zn + 3H_2O$, and dissolves in 53 parts of water at 15°; that of para-lactic acid crystallises with 2 molecules of water $(C_3H_5O_3)_2Zn + 2H_2O$, and dissolves in 17·5 parts of water at 14° to 15°.

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[1] *Zeitsch. angew. Chem.*, **15**, 172.

[2] *Chem Zentr.*, 1905, II., 988.

PART II

SYSTEMATIC COURSE OF QUALITATIVE CHEMICAL ANALYSIS

INTRODUCTION

WHEN the knowledge obtained by the study of the reactions of cations and anions is to be applied to the task of investigating the nature and composition of unknown substances, it is possible, in the case of a substance which is apparently from its external properties a simple individual one (as, for example, calc spar or copper sulphate), to confirm the observation by a few reactions whether the substance is, in fact, what it was taken to be. But since in most cases the nature of substances cannot be recognised by their mere appearance, and there is seldom, therefore, certainty that an individual substance is present, it is generally necessary to make use of a systematic course. That is to say, it is necessary to adopt a definite plan of applying the reactions in an appropriate sequence, in order that there may be certainty of discovering all substances which are present or may possibly be present.

If, in the hope of arriving more rapidly at a conclusion, one departs from this systematic course, analysis, instead of being an investigation based upon a scientific foundation and leading to certain conclusions, becomes mere guesswork, in which one frequently goes astray, on which much more time is spent than in the systematic process, and in which there is no certainty that some substance or other has not been entirely overlooked or confused with another through the false interpretation of reactions.

Obviously the known reactions of individual substances may be used in combination in different ways in a systematic process, and according to the conditions the preference may be given sometimes to one and sometimes to the other, in order to make the beginner conversant with the nature of the whole method of systematic qualitative analysis.

In practice it is necessary, in order to avoid the risk of overlooking some substance or other, to follow the systematic course point by point and not to omit any parts of it arbitrarily, unless the process itself indicates that they need not be used in a particular case. Experience will show how to proceed in testing associated compounds or mixtures for individual substances or groups of substances, or how, in such cases, the process may be shortened.

A description of analytical processes entails so many details, if no essential points are to be omitted, especially in the case of associated compounds, that it is easy to lose sight of the general outline. On the other hand, it is obviously necessary for intelligent work that the principle underlying the process, and the reasons why particular reagents are used and used in the order given, should be made clear. Hence, in the separate stages of the process we have generally prefixed the detailed description by an explanation of the fundamental principles of the process. In the case of associated compounds we have added to this explanation in every instance a tabular summary (for the cations), but give an express warning against an attempt to substitute this for the thorough description in practical work.

It is frequently possible to conclude from external conditions that the group of substances to be taken into consideration is only a limited one, or that the presence of certain substances will render the general course more difficult to carry out, or make it inadvisable. In such cases it is expedient to alter the course accordingly. Under other conditions, as *e.g.* in the presence of colouring, gelatinous, or insoluble organic substances, the general course of analysis cannot always be directly applied, but there must first be a preliminary treatment to destroy or remove the disturbing substances.

In order to give a comprehensive survey and to accustom the beginner to a definite method of working, a course of systematic analysis which has been tested by experience is given in the first chapter of this second part. This is restricted to the cations and anions of more frequent occurrence, the reactions of which have been described at length in the first part of this book.[1] It is so arranged that with accurate observation the end may be obtained rapidly and certainly. The outline has been so chosen that the essential points to be observed in carrying out analyses, and those which must be taken into consideration to avoid errors, have been given in detail. Further explanatory notes and observations are given in the third chapter, so as not to interfere with the general survey. In all cases where difficulties occur, or in which the reactions observed do not agree with the anticipated results, it is advisable always to refer to the corresponding places of this part of the book. In fact, we recommend that only when the course has become familiar through practice in numerous analyses, and a comprehensive grasp been obtained, should attention be given to these supplementary notes.

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[1] For other processes or for alterations in this course in the case of rare substances, reference may be made to the third chapter of this part.

The first chapter is divided into the following parts :—

1. Preliminary examination.
2. Solution.
3. Actual examination.

The last is further subdivided into the examination of simple compounds, in which only one cation and one anion are present, and that of associated compounds, *i.e.* of such substances (mixtures or compounds) in which all the cations and anions dealt with in this course may be assumed to be present.

The course relating to " simple compounds " is, strictly speaking, only of value as an introduction to the study of the subject, because in all practical cases it is never possible to be certain that several cations or anions are not present. It is, however, particularly useful for the purpose of gaining experience, as the conditions in connection with it are more simple.

In order to give data how to proceed in cases such as one of the three special instances mentioned on p. 545, some of the more important examples of frequent occurrence are given in the second chapter, and the methods to be used in their analysis are described in detail.

Finally, the third chapter has for its object the further explanation and amplification of the entire systematic process. These include—

1. Special notes and additions to the process given in the first and second chapters.

2. Directions inserted in smaller type how to alter or re-construct the process of analysis when it is necessary to take into consideration the presence of rare substances.

3. Outlines of analytical processes based upon other principles, either that another group classification is adopted from the first, or that only individual groups of substances are separated in another manner. In the case of these other analytical processes, it has obviously not been possible to deal with the details of the process as fully as in Chapters I. and II.

CHAPTER I.

PRACTICAL METHODS OF THE GENERAL COURSE.

1. PRELIMINARY EXAMINATION.[1]

IN the first place the external characteristics of the substance perceptible to the senses are noted: colour, form, hardness, density, odour, etc., since it is often possible to draw conclusions from these. **1.**[2]

Before going further, it is advisable to take into account what quantity of the substance under examination is available, so as to decide from the first what amount can be spared for the preliminary examination. Reasonable economy is necessary, even if large quantities are available; but the rule must be made, invariably to use only a portion of the substance for the examination, and to keep another portion in reserve, even though a small one, for unforeseen emergencies and for confirmatory tests.

A. THE SUBSTANCE UNDER EXAMINATION IS A SOLID.

SEC. 150.

1. It is neither in the form of a metal nor of an alloy.

General Survey.

The preliminary examination in this case consists in: 1. Finely powdering the substance under examination if necessary. 2. Determining its behaviour when heated in an ignition tube, in which process all possibilities from (*a*) to (*h*) are to be taken into consideration. 3 The phenomena on heating it in the reducing flame (*a*) to (*c*) and the flame coloration, if any. 4. These flame colorations are studied by means of fusion with phosphate beads.

Since the substance under examination may be mixed with different kinds of substances, it is not always possible in the tests described below to give sharply-defined instances. If, in the experiments, phenomena appear which are due to a combination of two or more circumstances, the conclusions to be drawn must naturally be adjusted.

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[1] *Cf.* the remarks in the third chapter of the second part, Nos. 1 to 5

[2] The numbers placed in the margin are intended to facilitate reference from one part of the course to another.

Process in detail.

2. 1. If the substance is in the form of powder or finely crystalline, it is suitable for examination; but if it is larger crystals or in lumps, a portion of it must be finely pulverised, if possible. In the case of softer substances this can be done in a porcelain mortar; but harder substances are broken into smaller pieces in a steel mortar or on an anvil, and then ground in an agate mortar.

3. 2. *A small portion of the powder is heated in a small glass tube 7 cm. long and 5 mm. wide, which is fused at one end or has a small bulb blown upon it.* (Under certain conditions this may be done upon a crucible lid or in a small basin, see (Chap. III., No. 3[1]). This should be done moderately at first, subsequently strongly in a gas flame.[2] The resulting phenomena enable many conclusions to be drawn with certainty, and others with probability as to the nature of the substance. Those to which the principal attention has to be given are grouped together under the following headings, several of which frequently refer to the same substance.

(*a*) *The substance remains unchanged* No organic substances, no salts containing water, no readily-fusible substances, no volatile substances (with the exception of carbon dioxide, *i.e.* carbonate ion, since a perceptible alteration often takes place when the gas escapes), are present.

4. (*b*) *The substance changes colour without melting at a moderate heat*[3] A change from white to yellow, becoming white again on cooling, indicates *zinc oxide* or *zinc salts*; from white to yellowish-brown, becoming dirty pale yellow on cooling, indicates *tin oxide* or *tin salts*; from white or reddish-yellow to brown-red, becoming yellow on cooling, fusible at red heat, indicates *lead oxide* or *lead salts;* from white or pale yellow to orange-yellow or red-brown, becoming pale yellow on cooling, fusible at strong red heat, indicates *bismuth oxide* or *bismuth salts;* from white or yellowish-white to dark brown, remaining dark brown on cooling, indicates *manganous oxide* or *manganous salts;* these last colours becoming, as a rule, light reddish-brown on cooling, indicate *cadmium oxide* or *cadmium salts;* from light blue or light green into black, with the simultaneous liberation of water, indicates *cupric hydroxide* or *carbonate*, and also the corresponding *nickel compounds;* from greyish-white to black indicates *ferrous carbonate;* from brown-red to black, becoming brown-red again on cooling, indicates *ferric oxide;* from yellow to dark orange, fusible at a strong heat, indicates *potassium chromate;* from light red to dark red and then violet-black, becoming light red again on cooling, and yielding a sublimate of mercury on stronger ignition, indicates *mercuric oxide:* from light red to brown, cooling to light red, indicates *red lead*, which, when strongly heated, yields a yellow fusible residue of lead oxide, etc.

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[1] In referring to the marginal numbers of the third chapter, the prefix "No." is always used.

[2] *Cf.* Sec. 13 and Sec. 19.

[3] The significance of the change of colour needs care in its interpretation; thus the absence of a metal must not be inferred from the absence of an alteration of colour, since although its salts may show the particular change of colour, it depends upon the anion present whether or no it occurs; for example, lead sulphate remains unchanged on heating.

5. (*c*) *The substance melts without emitting water vapour.* If, on stronger heating, a gas (oxygen) is evolved and a fragment of charcoal, thrown into it, burns with violence, the presence of *nitrate* or *chlorate* is indicated.

6. (*d*) *Water escapes and condenses in the colder part of the tube.* This indicates (1) *Substances containing water of crystallisation* (many of these melt readily and solidify again after the escape of the water; many swell up considerably on liberation of the water, *e.g* borax, alum); (2) Salts containing decomposable *perhydrates*, *hydroxides*, or *hydrates* (the substances often do not melt); (3) Anhydrous salts, between the lamellæ of which water is *mechanically enclosed* (the substances decrepitate); (4) Substances to which external *moisture* is attached; or (5) *Ammonium salts, which are decomposed with the formation of water, e.g.* ammonium nitrate, in the decomposition of which nitrous oxide gas is simultaneously evolved (ignites a glowing match). The drops of water condensed in the tube are tested as to their reaction. If this is alkaline, ammonium ion is indicated; if acid, the anion of a volatile acid (sulphuric acid, sulphurous acid, hydrofluoric acid, hydrochloric, hydrobromic, or hydriodic acid, acetic acid, etc.).

7. (*e*) *The substance decrepitates or decomposes without liberation of water.* This points to the presence of certain anhydrous minerals which have this property, *e.g.* heavy spar, zinc blende, lead glance, spathic iron ore, plumbocalcite, etc.

8. (*f*) *Gases or vapours are evolved.* A note is taken whether they have a colour, odour, acid or alkaline reaction, or are combustible, etc.

(*aa*) *Oxygen* indicates oxides or "noble" metals, peroxides, per-salts, chlorates, nitrates. A glowing match is rekindled in the current of the gas (see also 5).

(*bb*) *Sulphur dioxide.* This is produced in the decomposition of sulphites of heavy metals, and also of many sulphates, as well as in the ignition of mixtures of sulphides with sulphates. It may be recognised by its odour and acid reaction.

(*cc*) *Nitrogen trioxide or tetroxide* derived from the decomposition of nitrites or nitrates, especially those of the heavy metals. They may be recognised by their brownish-red colour and the odour of their vapours.

(*dd*) *Carbon dioxide* points to the presence of carbonates decomposed on heating, or to the oxalates of reducible metals, *e.g.* cupric oxalate. The gas is colourless odourless, and non-combustible. A drop of lime water exposed to a current of the gas on a glass rod or clock glass becomes turbid.

(*ee*) *Carbon monoxide* points to the presence of oxalates or also of formates. The gas burns with a blue flame. If carbon dioxide is mixed with it, as, for example, when magnesium oxalate or formates of easily reducible metals are present, it is difficult to ignite. In the case of formates, there is often considerable carbonisation. Oxalates, when mixed on a clock glass with manganese dioxide (free from carbonate), a little water and concentrated sulphuric acid, evolve carbon dioxide, whereas this is not the case with formates.

(*ff*) *Chlorine, bromine, or iodine* indicates the presence of chlorides, bromides, or iodides, decomposable with the liberation of the halogens. The gases may be readily recognised by their colour (yellowish-green, brownish-red, violet) and their odours; a black sublimate is formed if any considerable quantity of iodine is liberated (*cf.* 9).

(*gg*) *Cyanogen and hydrogen cyanide* indicate the presence of cyanogen compounds, which are decomposed on heating[1] (*e.g.* mercuric cyanide, Prussian blue). Both may be recognised by their odours, and cyanogen, when it is fairly pure, by the fact that it burns with a carmine red flame[2] (*cf.* also Sec. 154, 33, *g*).

(*hh*) *Hydrogen sulphide* points to the presence of hydrated sulphides (also of thiosulphates). It is readily recognised by its odour.

(*ii*) *Ammonia* may be derived from the decomposition of ammonium salts, or also of hydrated cyanogen compounds or nitrogenous organic substances, in which last case darkening or carbonisation occurs, whilst, as a rule, malodorous combustible oils also escape with the ammonia.

(*kk*) *Hydrocarbons and other gaseous organic compounds* indicate the presence of organic substances, *i.e.* in the case of those compounds which are being dealt with here,[3] *organic acids* or their salts. The gases usually have an empyreumatic odour and generally burn with a luminous flame (*cf.* 10).

(*g*) A sublimate is formed[4] (*cf.* Chap. III., No. 2, last paragraph). **9.**
The presence of volatile substances is indicated.

The following are of more frequent occurrence:—

(*aa*) *Sulphur*, from mixtures or metal sulphides. Reddish-brown drops; when cold, yellow or yellowish-brown solid.

(*bb*) *Iodine*, from mixtures, many iodides, iodic acid, etc. Vapour violet; sublimate black; iodine odour.

(*cc*) *Ammonium salts*. White sublimates Heated with sodium carbonate and a drop of water, evolve ammonia.

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[1] *Cf.* also Chap. III., No. 2, last paragraph.

[2] It may be noted here that insoluble cyanogen compounds are examined by a special method (Sec. 180).

[3] *Cf.* Chap. III., No. 3.

[4] See Sec. 14

(*dd*) *Mercury* and its compounds. Metallic mercury forms minute globules; mercuric sulphide is black, becoming red when heated; mercuric chloride melts before volatilising, emits dense vapours, and forms a white sublimate; mercurous chloride sublimes without previously melting, to form a sublimate which is yellow while hot and white when cold; red mercuric iodide yields a yellow sublimate.

(*ee*) *Arsenic* and its compounds. *Metallic arsenic* forms the well-known mirror; *arsenic trioxide* yields lustrous, minute crystals; the *sulphides of arsenic* form sublimates which are reddish-yellow while hot, and yellow or yellowish-red when cold.

(*ff*) *Antimony trioxide* melts to form a yellow liquid before subliming. The sublimate consists of lustrous needles.

(*gg*) *Lead chloride* melts to a yellow liquid before forming a sublimate. The sublimate is white, and volatilises with difficulty.

(*hh*) *Benzoic acid*, *succinic acid*, *cinnamic acid* form white crystalline sublimates; the acids prepared from gum benzoin, or amber, are not quite pure; they may be recognised by the odour of the vapours.

(*ii*) *Salicylic acid* gives a white, crystalline sublimate. When rapidly and strongly heated an odour of phenol is produced.

(*kk*) *Oxalic acid* gives a white, crystalline sublimate; when heated in a small tube it produces dense vapours which have an irritating action upon the throat. On heating a small quantity with a drop of concentrated sulphuric acid on platinum foil, an abundant evolution of gas is produced.

10. (*h*) *Carbonisation occurs.* This indicates organic substances[1] Combustible gases, usually with an empyreumatic odour (in the case of acetates, acetic acid, or acetone), and water are also always produced, the latter having an acid or alkaline reaction. Tarry products of distillation are also almost invariably deposited in the upper part of the tube. An odour of burnt hair indicates the presence of nitrogenous organic substances, especially proteins. If the residue effervesces when treated with acids, whilst the

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[1] *Cf.* Chap. III, No. 3.

original substance does not show this phenomenon, it indicates that alkali or alkaline earth salts of organic acids are present.

(*i*) *A metal is left.* This indicates the presence of carbonates or oxides of noble metals or salts of easily reducible metals with organic acids[1] (*e.g* cupric acetate). In this case under certain conditions little, if any, carbon is produced (*h*).

3. *A small portion*[2] *of the substance is introduced into a hollow on* **11.** *charcoal* and submitted to the inner blowpipe flame.[3] Since the reactions which occur largely re-duplicate those already observed when the substance was heated in a glass tube, only those characteristic of this method of treatment will be given here. If sulphur dioxide is developed when the flame is directed on to the charcoal, *sulphur* or a *sulphide* is indicated; if a garlic-like odour of arsenic is produced, the presence of arsenic or an arsenic compound is indicated; if there is an odour of ammonia, the presence of certain ammonium compounds, *e.g.* ammonium carbonate, is indicated; if the carbon burns vigorously, substances which emit oxygen, usually nitrates, chlorates, or peroxides, are present. Care should be taken to avoid breathing the vapours from substances which, when heated in glass tubes, have yielded vapours or sublimates (Chap. III., No. 2, last paragraph).

In addition to the tests described, definite conclusions may also be drawn to some extent from the following phenomena:—

(*a*) *The substance melts and spreads on the charcoal or forms a* **12.** *bead in the hollow*, without a simultaneous deposit. This primarily indicates alkali salts.

(*b*) *An infusible white residue* remains on the charcoal, either at **13.** once or after previously melting in the water of crystallisation. This indicates especially alkaline earth metals, aluminium, and zinc, which are present in the form of their oxides or of salts which are stable on heating (zinc oxide appears yellow while hot), and also indicates silicon dioxide. Of these *strontia*, *lime*, *magnesia*, and *zinc oxide* are characterised by emitting an intense light in the blowpipe flame, and alkaline earth metal compounds by the fact that their oxides or sulphides show an alkaline reaction after moistening the residue. A drop of cobaltous nitrate solution is placed on the infusible ignited white mass and the latter again strongly heated. Various colorations are thereby produced, of which the following in particular are characteristic and easily recognised. A fine blue coloration indicates *aluminium* (*oxide*) and *silicon dioxide*,[1] a green coloration indicates *zinc* (*oxide*), and a violet coloration *magnesium phosphate* or *arsenate*. In the presence of many *phosphates* of alkaline earths a more or less pronounced blue coloration is also obtained, of which note should be taken.

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[1] *Cf.* Chap. III., No. 3.

[2] If there is no incandescence, etc., when the substance is heated on charcoal, a larger amount may be used for the experiment.

[3] *Cf.* Sec. 20; also Chap. III., No. 4.

In the case of (*a*) or (*b*) the preliminary examination is completed by determining the *flame coloration* (especially in testing for alkali and alkaline earth metals). A little of the substance is placed on a loop of platinum wire (preferably slightly moistened), touched with hydrochloric acid, carefully dried near the edge of the flame, again moistened with hydrochloric acid, and introduced into the fusion area of a Bunsen flame. Flame colorations, due to alkali metals, are first produced, and then, after volatilisation of the alkali metals, the colorations due to barium, strontium, or calcium. Sometimes it is advisable to ignite the substance first in the reducing flame, and then to moisten it with hydrochloric acid, *e g.* when sulphates are present.

If a flame coloration appears, the following specific conclusions may be drawn from it :—

A *yellow* flame indicates *sodium*.
A *violet* flame indicates *potassium*, *cæsium*, *rubidium*.
A *yellowish-red* flame indicates *calcium*.[2]
A *red* flame indicates *lithium*, *strontium* (*calcium*).[3]
A *green* flame indicates *thallium*, *boric acid*, *copper*.
A *yellowish-green* flame indicates *barium*.
A *blue* flame indicates *indium*, *copper* (as chloride or bromide).
A *pale-blue to blue-green* flame indicates *arsenic*, *antimony*.

For further particulars, see Secs. 22, 31, and 38.

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[1] This conclusion is only justifiable when an infusible substance is actually present. Fused masses are also frequently coloured blue by cobalt.

[2] Or a metal which colours the flame red in the presence of sodium.

[3] The calcium coloration is much redder in the absence of sodium, especially when hydrochloric acid is present, than is usually assumed to be the case.

(*c*) *A residue of a different colour is left, a reduction to metal takes place, or a deposit is formed.* In this case a conclusion cannot immediately be drawn from the reaction which has occurred, but in order to bring about decisive phenomena a small portion of the powder is mixed with a drop of water and sodium carbonate (an odour of ammonia at this stage indicates the presence of an ammonium compound), heated on charcoal in the reducing flame of the blowpipe, and a note taken of any residue in the hollow of the charcoal and of any deposit on the surface of the charcoal. If a sulphide or arsenide is present (see 11), or if the substance contained much water of crystallisation, it should be heated first for a short time on the cover of a porcelain crucible, and the residue ground up and mixed with sodium carbonate. If only an incomplete reduction to metal occurred, it is advisable to repeat the test once more by adding a little potassium cyanide to the substance which has been mixed with sodium carbonate, or the substance may be mixed with sodium formate, since this materially facilitates the reduction to metal. **14.**

If a reduction to metal has occurred, the residue is moistened with water, cut out, ground up in a small mortar, and the particles of charcoal washed away. By this means gold is obtained in yellow flakes, copper in copper-red ones, silver in nearly white, tin in greyish-white, and lead in whitish-grey flakes, whilst bismuth is left as a reddish-grey powder, zinc as a bluish-white, and antimony as a grey powder. If copper and tin or copper and zinc are present together yellow alloys are sometimes formed.

The following specific phenomena may be noted :—

(*α*) A granule of metal obtained after thorough blowpipe treatment without a deposit being formed on the charcoal points to the presence of *gold* or *copper*. The latter may also frequently be recognised by the green coloration of the flame. Platinum, iron, cobalt, and nickel compounds are also reduced, but do not yield metallic granules, at all events when they are not present together with compounds of other metals. **15.**

(*β*) A deposit is formed upon the charcoal, with or without the simultaneous production of a granule of metal. **16.**

(*aa*) A white deposit at a distance from the substance, and volatilising very readily with the emission of a garlic-like odour indicates *arsenic*.

(*bb*) A white deposit not far distant from the substance, and capable of being moved from one part to the other, indicates antimony. As a rule dark dull granules of metal will be simultaneously noticed, which continue to emit white fumes after the blowing has stopped, and on cooling become enveloped with crystals of antimony oxide; the granules are brittle.

(*cc*) A deposit which is *yellow* while hot and white on cooling, is fairly close to the substance, volatilises with difficulty, and, when heated with cobaltous nitrate solution, shows a green coloration, indicates zinc.

(*dd*) A pale *yellow* deposit while hot and white on cooling, which lies close to the substance and cannot be volatilised in any flame, indicates *tin*. The metal granules which are formed simultaneously, although only in a good reducing flame, are bright, readily fusible, and malleable.

(*ee*) A *lemon-yellow* deposit while hot and sulphur-yellow on cooling, and which when heated in the reducing flame leaves a blue shimmer in its place, indicates *lead*. The granules of metal formed at the same time are readily fusible and malleable.

(*ff*) A deposit which is dark *orange-yellow* while hot and lemon-yellow on cooling, and which when heated in the reducing flame leaves no blue shimmer in its place, indicates *bismuth*. The granules of metal simultaneously formed are readily fusible and brittle.

(*gg*) A deposit which is *reddish-brown*, and *orange-yellow* in thin layers, and volatilises without leaving a coloured shimmer, indicates *cadmium*.

(*hh*) A faint *dark red* deposit, with the simultaneous formation of white granules of metal, indicates *silver*. If lead and antimony are also present the deposit is crimson.

17. (γ) The formation of *sodium sulphide*, which may be readily identified as in Sec. 105, 9, indicates *sulphides*, *sulphates*, or also *sulphites*.

4. *A small portion of the substance is fused with an alkali phosphate bead (see Sec. 21), is exposed for some time to the oxidising flame and observed both while hot and after cooling, and if any coloration has been produced it is also heated in the reducing flame.*

(*a*) *The substance is dissolved readily and in considerable quantity, forming a bead, which is transparent while hot.*

(α) The colour of the bead is:— **18.**

blue: *cobalt* is indicated.

green, becoming blue on cooling and in the upper reducing flame red after cooling, although only when thoroughly saturated: *copper* is indicated.

green, particularly fine on cooling, and unchanged in the reducing flame: *chromium* is indicated.

brownish-red, becoming pale yellow or colourless on cooling; in the reducing flame red while hot and yellow on cooling, and then greenish: *iron* is indicated.

ruby-red, becoming blue and then colourless: *gold* is indicated (Sec. 81, 11); *reddish* to *brownish-red*, becoming paler on cooling, and then yellow to reddish-yellow or even colourless and unchanged in the reducing flame: *nickel* is indicated.

fawn-coloured: *platinum* is indicated (Sec. 85, 15).

yellowish brown, becoming light yellow to colourless on cooling, and in the reducing flame (preferably after treatment with tin) almost colourless, and blackish-grey on cooling: *bismuth* is indicated.

pale yellow to *opal-coloured*, somewhat turbid on cooling, and whitish-grey in the reducing flame: *silver* is indicated.

amethyst-coloured, especially after cooling in the outer flame, colourless in the reducing flame, and not quite clear: *manganese* is indicated.

(β) *The hot bead is not coloured.* **19.**

(*aa*) *It remains clear on cooling.* This indicates *antimony*, *aluminium*, *alkali compounds*, *zinc*, *cadmium*, *lead*, *calcium*, and *magnesium* (the five last yield on the addition of a considerable quantity enamel-white beads. In the presence of lead the saturated bead is yellowish).

(*bb*) *It becomes enamel-white on cooling, even in the presence of a small quantity of the substance.* *Barium* or *strontium* is indicated.

20. *(b) The substance dissolves with difficulty and only in slight quantity.*

(*α*) *The bead is colourless and also remains clear on cooling. The undissolved portion appears semi-transparent*; on the addition of a little ferric oxide the glass assumes the colour of an iron bead. *Silicon dioxide* is indicated (or a *silicate*). The reaction takes place better on the use of not too small a granule or fragment than when fine powder is used. Its non-occurrence does *not* justify the conclusion that silicic acid is absent (*cf.* Sec. 115, 9).

(*β*) The bead is colourless, and remains so, even after the addition of ferric oxide. *Tin* is indicated.

21. (*c*) The substance does not dissolve at all and floats (as metal) in the bead. *Gold* or *platinum* is indicated.

When the preliminary examination is finished the substance under examination should be dissolved as in Sec. 154 (32) or Sec. 155 (34).

SEC. 151.

(2) The substance is an elementary metal or an alloy.

22. 1. *A portion is mixed and heated with water, to which a little acetic acid has been added.* The evolution of hydrogen indicates the presence of a light metal (possibly also that of elementary manganese).

23. 2. *A portion is heated in a hollow on charcoal in the inner blowpipe flame*, and a note taken whether the substance melts, or a deposit is formed, or an odour produced, etc.

The following metals may thus be recognised with more or less certainty: *arsenic* by its odour of garlic; *mercury* by its ready volatility; *antimony, zinc, lead, bismuth, cadmium, tin,* and *silver* by their fusibility, with the formation of deposits on the charcoal (*cf.* 16); *copper* by the green coloration of the outer flame. Only when a single pure or nearly pure metal is present can any further conclusions be drawn; thus *gold* melts without a deposit, whilst *platinum, iron, manganese, nickel,* and *cobalt* do not melt in the blowpipe flame if they are pure.

24. 3. *A small portion is heated in a glass tube fused together at one end in a gas flame, the action of which is intensified by the use of a chimney.*

(*a*) *No deposit is formed in the colder part of the tube.* Mercury is absent.

(*b*) *A deposit is formed. Mercury*, *cadmium*, or *arsenic* is present. The deposit of the first metal, which consists entirely of small globules, cannot readily be confused with the cadmium or arsenic deposit. The non-occurrence of deposits, however, is not necessarily conclusive of the absence of cadmium or arsenic.

After the preliminary examination is finished the substance under examination should be dissolved as in Sec. 156 (42).

Sec. 152.

B. The Substance under Examination is a Liquid.

1. *A small portion is heated* in a platinum or porcelain basin and note taken whether the liquid can be evaporated without leaving a residue, *i.e.* whether a solution of a solid substance is present. If this is the case, the residue is tested as in Sec. 150. If the liquid evaporates without leaving a residue there may be present (if the reaction is acid, (27)) volatile acids (hydrochloric, nitric, acetic, formic acids, etc.), and if the reaction is alkaline the solution may contain ammonia. In this case the odour affords a further indication, especially when the liquid is heated. If it is *not* a solution, organic substances will almost invariably be present when the liquid was not merely water. In this case reference may be made to what is said in Chap. III., No. 3. If a liquid metal (mercury) is present, it should be treated as described in the previous sections. **25.**

2. *The odour of the liquid* or of the vapours which escape when it is heated usually give a sufficient indication of the nature of the solvent. If necessary a *distillation* is made, a note being taken of the temperature at which the vapours distil (Sec. 12). If an aqueous solution (which may contain volatile acids or ammonia) is not present, simple solvents such as alcohol, ether, etc., may be evaporated, and the residue, if it is of an inorganic nature, examined by the same method as was previously used when a solid substance was present, *i.e.* beginning with Sec. 150. **26.**

If the residue contains organic substances, and it is not possible to decide by other means that it belongs to the organic acids dealt with in this book (or alkaloids, *cf.* Sec. 209 *et seq.*), or that the case comes within the scope of those dealt with in

Sec. 196 *et seq.*, reference should be made to Chap. III. No. 3. This also applies to the determination of the nature of the solvent.

27. 3. *A test is made with litmus paper.*

(*a*) *Blue paper becomes red.* This reaction may be due either to an acid or an acid salt, or to a salt which has undergone hydrolytic dissociation when dissolved in water. To decide which is the case, a small portion of the liquid is poured on to a clock glass and the extreme tip of a glass rod, moistened with a dilute solution of sodium carbonate, introduced into it; if the liquid remains clear, or any precipitate formed dissolves on stirring, the former alternative is the case, whilst if a permanent turbidity is produced the latter is generally the case.

28. (*b*) *Reddened litmus paper becomes blue.* This indicates hydroxides, carbonates, or sulphides of alkali or alkaline earth metals (and of ammonium), also the salts of other weak acids with alkali or alkaline earth metals (especially alkali borates) which have undergone hydrolytic dissociation; basic lead acetate, thallium, hydroxide, and carbonate also show an alkaline reaction in aqueous solution owing to hydrolysis.

29. 4. If the solution is an aqueous one and has an acid reaction, *a small portion of it is diluted with much water.* If this produces a milky turbidity the ions of *bismuth, antimony* (possibly also of tin or lead) are indicated, *cf.* Sec. 76, 3, and Sec. 91, 4.

30. After the preliminary examination is completed the actual tests are made If the solution is an aqueous one and has a neutral reaction it can only contain substances soluble in water; if, however, it has an acid reaction (this being due to the presence of an acid), it is necessary to take into consideration in the actual tests not only substances which are soluble in water, but also those which dissolve in acids. Bearing these facts in mind, the examination is continued at Secs. 157, 158, or 159, or Secs. 160, 161, or 162, provided the assumption that only one cation and one anion is present is justified; but if there is no such justification, tests are made as described in Secs. 164, 175, or 176, or in 177 or 178. If liquids have an alkaline reaction, the examination is made as in Secs. 157, 158, or 159, provided it may be assumed that only one cation and one anion is present; otherwise as in Secs. 164, 175, or 176.

II. SOLUTION OF SUBSTANCES OR THEIR CLASSIFICATION ACCORDING TO THEIR BEHAVIOUR TOWARDS CERTAIN SOLVENTS.[1]

SEC. 153.

General Survey

The media which we use for classifying simple substances or **31.** compounds in accordance with their solubility, or of separating them when mixed together, are water and acids (hydrochloric acid, nitric acid, *aqua regia*). According to their behaviour towards these solvents substances may be divided into three classes—

First class.—Substances soluble in water

Second class.—Substances practically insoluble or dissolving with difficulty in water, but soluble in hydrochloric acid, nitric acid, or aqua regia.

Third class.—Substances practically insoluble or dissolving with difficulty in water, and also in hydrochloric acid, nitric acid, and aqua regia.

Metals or metal alloys are more suitably dissolved by a somewhat different method, and a special method for their treatment is, therefore, given (Sec. 156)

Procedure in detail.

To effect the solution or test the solubility of a substance, the following method is employed :—

A. THE SUBSTANCE IS NEITHER AN ELEMENTARY METAL NOR AN ALLOY.

Simple Compounds.[2]

SEC. 154.

If it is a question of a simple compound, the solubility class to **32.** which it belongs is first determined. For this purpose a small sample is treated with about ten times its quantity of distilled water, and then, if necessary, with *dilute* hydrochloric acid (*i.e.* hydrochloric acid of sp. gr. 1·12 mixed with about three times its quantity of water), with concentrated hydrochloric acid, with nitric acid,[1] and with *aqua regia successively in the order given*, first without and then with the aid of heat. If the small sample can be dissolved[2] by one of these solvents, a somewhat larger quantity (about 1 grm.) is treated in the same way, and tests are applied to aqueous solutions in accordance with Secs. 157, 158, or 159, to acid solutions as in Secs. 160, 161, or 162, and to substances insoluble or practically insoluble in acids in accordance with Sec. 163.

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[1] See also the remarks in Part II., Chap. III., Nos. 6 to 8.

[2] This name has been adopted for the sake of brevity for such compounds as contain only one cation and one anion.

It should be noted that *simple* compounds must dissolve completely in *one* solvent. If small particles remain undissolved they usually consist of impurities which may be ignored (*cf.*, however, 33 (*b*), (*c*), and (*d*)), and in *such* cases the substances are *not* treated as though insoluble in acid.

33. On dissolving the substance in acids a series of phenomena may be produced, *of which especial notice must be taken.*

(*a*) *Effervescence* indicates carbonates (the liberated carbon dioxide may be identified according to Sec. 111, 4); or sulphides, in which case the liberated hydrogen sulphide may be identified by its odour.

(*b*) *Separation of sulphur*, which may be easily recognised by its appearance, colour, and specific gravity, and can usually be filtered off after being boiled for some time, indicates sulphides The filtered solution is diluted[3] and tested according to Sec. 160, whilst the residue may be examined according to Sec 163.

(*c*) Separation of *silicic acid*, usually in gelatinous form, indicates silicates. These are examined by a special process, Secs. 181 to 183 (*cf*., however, Chap. III., No. 7).

(*d*) Separation of *crystalline benzoic acid*, *salicylic acid*, or *cinnamic acid* can only occur when the preliminary examination has indicated the presence of organic substances. (If any doubt exists as to whether the salt has dissociated with solution of the cation, the solution is shaken with ether, which will dissolve the organic acid, so that two clear layers of liquid will be obtained.) For the detection of the cation a fresh quantity of the original substance is treated with acid, diluted with a little water if necessary, and the liquid filtered from the separated organic acid. The filtrate is tested as described in 47 (*b*), footnote.

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[1] Sometimes, *e.g.* in the case of barium compounds, a substance does not dissolve completely in acids, owing to the formation of a substance which is less soluble in the acid than in water. In such cases complete solution is effected by diluting the liquid with water.

[2] If an organic substance is present, it may belong to the class of substances soluble in water, notwithstanding the fact that it cannot be completely dissolved either by treatment with water or with acids. It belongs then to the cases mentioned in 33 (*d*).

[3] A turbidity at this point points to the presence of bismuth or antimony compounds (possibly also of tin or lead compounds). In the case of the former the turbidity is removed by the addition of hydrochloric acid.

(*e*) Evolution of *chlorine* (*when hydrochloric acid is used*) indicates the presence of oxidising substances: peroxides, per-salts, chromates, chlorates, etc.

(*f*) The evolution of *nitric oxide* or *nitrogen trioxide* when *nitric acid* is used points to the development of an oxidation process, whilst bromine or iodine vapour indicates bromides or iodides.

(*g*) Development of an *odour of hydrocyanic acid* indicates the presence of cyanogen compounds, insoluble in water. A suitable special method of examining these is given in Sec. 180.

In many cases (with ferro- and ferricyanides) a blue or green coloration is simultaneously produced on heating the substance with hydrochloric acid.

If there is any doubt as to the evolution of hydrocyanic acid, a *small* quantity of the substance may be heated with sulphuric acid or fused in an ignition tube with potassium hydrogen sulphate and the liberated vapour made to act upon a strip of paper which has been saturated with a solution of a ferrous and ferric salt, and then dipped in alkali hydroxide solution. On subsequently moistening this with hydrochloric acid the formation of Prussian blue indicates the presence of cyanogen (*cf.* Sec. 120, 7).

Mixed Compounds.[1]

SEC. 155.

If a mixed compound is to be examined, it is advisable, if necessary, to begin by separating the substances from one another into their respective solubility classes. For this purpose the following procedure is adopted:— **34.**

1. A sample (about 1 to 3 grms.) of the substance under examination is treated in the form of powder with about 10 times its quantity of distilled water in a flask and the mixture heated to boiling point.

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[1] This name is applied here and in the following pages to compounds and mixtures in which all the cations and anions of more frequent occurrence may be present.

35. (*a*) *A clear solution is obtained.* In this case the whole of the compounds in the first solubility class have to be taken into consideration, without, however, overlooking what has been said about the reactions in the preliminary examination (30). Tests are applied for the detection of the cations as in Sec. 164, and for the detection of the anions as in Secs. 175 and 176.

36. (*b*) *A residue is left, even after long-continued boiling.* It is allowed to subside and the liquid filtered, the insoluble matter being left, as far as possible, in the flask. A sample of the clear filtrate is evaporated in a platinum or porcelain basin or in a clock-glass (*cf.* Chap. III., No. 6, and in particular the footnote). If a residue is left, part of the substance is soluble in water. The residue is repeatedly boiled with fresh portions of water, in order to bring the soluble constituents as completely as possible into aqueous solution,[1] and tests are applied to this solution as described in (35) and to the insoluble residue as in (37).

37. 2. The substance which is insoluble in water, or which has been extracted as completely as possible with water, is separated by decantation or filtration from the liquid, and a portion treated with *dilute* (*cf.* 32) hydrochloric acid. If it is insoluble or not completely soluble the acid is boiled; and if still there is not complete solution the liquid is poured off into another flask, the residue boiled with concentrated hydrochloric acid, and if a solution is obtained it is added to the liquid previously decanted.

With regard to the phenomena which may occur during the treatment with hydrochloric acid, see (33).

38. (*a*) *Complete solution is effected by the treatment with hydrochloric acid* (or only sulphur, silicic acid, benzoic acid, salicylic acid, or cinnamic acid separates, *cf.* 33). The substances insoluble in water then belong to the second solubility class. The examination is continued according to Sec. 165. Any deposit which appears to be sulphur should be submitted to further examination, as in Sec. 179. If silicic acid has separated, the liquid is evaporated to dryness, in order to convert this completely from the colloidal condition into insoluble silicon dioxide, as described in Sec. 181, and the residue moistened with hydrochloric acid, treated with water and filtered. The filtrate is subsequently examined as in Sec. 165 *et seq.* The residue is tested to see whether it contains any substances in addition to silicon dioxide, insoluble in acid. *Cf.* in this connection Chap. III., No. 7. Any separated organic acids are filtered off, and tested as described in Sec. 159 for cinnamylate, succinate, and salicylate ions.

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[1] If substances, such as calcium sulphate or lead chloride, which are only sparingly soluble in water, are present, it is sufficient to boil the residue four times with water, since complete extraction can only be effected with difficulty.

(*b*) *A residue is still left.* In this case the flask containing the portion which has been boiled with hydrochloric acid is put aside for a time.[1]

3. If the substance which was insoluble in water, or has been extracted therewith as far as possible, is not completely dissolved by hydrochloric acid, a further portion is heated with *nitric acid* and subsequently diluted with water. **39.**

With regard to the phenomena which may occur, see (33).

(*a*) *Complete solution is effected by nitric acid* (or only sulphur, silicic acid, or an organic acid separates, *cf.* 33). The substances insoluble in water belong also in this case to the second solubility class. The nitric acid soluton is examined as in Sec. 164, III., (109), and in general as described in (38).

(*b*) *There is still an insoluble residue on heating the substance with nitric acid, even after dilution with water.* The examination is continued as in (40).

4. If the substances insoluble in water do not dissolve completely either in hydrochloric or in nitric acid, an attempt is made to dissolve them in *aqua regia* (*cf.* p. 19). For this purpose the contents of the flask in which nitric acid has been tried as a solvent are mixed with those of the flask in which concentrated hydrochloric acid was tried, and the mixture gradually heated and finally gently boiled. If complete solution does not take place, the clear liquid is poured off and the residue kept moderately boiling for some time with concentrated *aqua regia*. Finally the more dilute *aqua regia* solution which was poured off, and also the solution in dilute hydrochloric acid which was poured off in (37) are added. After the whole has again been gently boiled, a note is taken whether complete solution has occurred, or **40.**

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[1] In many cases the residue left after the treatment with hydrochloric acid dissolves when diluted with water, *e.g.* in the presence of barium salts (p. 562, footnote 1); naturally the case then comes under the heading (*a*).

whether a residue insoluble in *aqua regia* is left. In the *latter* case the solution is filtered, after dilution with a little water if necessary,[1] the residue washed with boiling water, and the washings added to the filtrate and examined as in Sec. 165. In the *former* case the clear solution[2] is treated in the same way (in this connection *cf.* Chap. III., No. 6, last paragraph).

41. 5. If *aqua regia* leaves a residue after boiling, this residue is thoroughly washed with boiling water and examined as in Sec. 179.

B. THE SUBSTANCE IS A METAL OR A METAL ALLOY.

SEC. 156.

General Survey.

42. Elementary metals are best classified in accordance with their behaviour towards nitric acid as follows:—

I. *Metals which are not attacked by nitric acid:* Gold, platinum.

II. *Metals which are oxidised by nitric acid, but the oxides of which do not dissolve* (to any appreciable extent) *either in excess of acid or in water:* Antimony, tin.

III. *Metals which are oxidised by nitric acid, and converted into nitrates soluble in excess of acid or in water:* All the rest.

Since it is only very occasionally that an analysis of chemically pure elementary metals is required (for nearly all commercial metals are not chemically pure, but contain larger or smaller amounts of other elements) separate directions for the treatment of metals and alloys are not given in the following pages, but only the latter are dealt with, since the method is applicable under all conditions, whether actual alloys, impure metals, or pure metals are present. With regard to the quantities to be taken for the treatment with nitric acid very small fragments are sufficient in the case of pure metals, whilst samples of 1 to 3 grms. should be used for the detection of the individual constituents of alloys, *i.e.* for analyses in which minute quantities of metals present as impurities may be ignored. If, however, tests are to be applied for the metallic impurities which are usually only present in traces in the metals obtained by metallurgical processes, as, for example, in testing soft lead for bismuth, copper, antimony, iron, zinc, silver, etc., quantities of 100 to 200 grms. must be taken for the analysis.

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[1] A turbidity at this stage usually indicates the presence of bismuth or antimony compounds; it may be removed by the addition of hydrochloric acid.

[2] If pointed crystals separate from the acid solution on cooling, they will usually consist of lead chloride. In such cases it is often advantageous to decant the liquid from the crystals and examine the latter separately.

If metastannic chloride has been formed during the boiling with *aqua regia* the washing water which dissolves this salt becomes turbid when it falls into the strongly acid liquid first passing through the filter. In that case the washing water is collected in a separate vessel, and the two solutions separately treated with hydrogen sulphide (Sec. 165), but filtered through the same filter.

Method of Solution.

The sample is heated with nitric acid of sp. gr. 1·2, to which, if lead nitrate separates, an equal volume of water is added.

1. *There is complete solution, or it can be effected by the addition of water* (Chap. III., No. 8). This indicates the absence of platinum[1] and gold, antimony[2] and tin. The procedure described in Sec. 160 or Sec. 161, III., (109), is followed according to whether one or several metals are present. **43.**
2. *A residue is left:* **44.**

   It is filtered off and washed, and the filtrate examined as in Sec. 161, III., (109), provided that a test shows that it contains anything in solution.

   (*a*) The residue is *metallic*. It is dissolved in *aqua regia*, and the solution tested for *gold* and *platinum* (Sec. 86).

   (*b*) The residue is *white* and *pulverulent*. This usually indicates the presence of *antimony* or *tin*. If there is reason for concluding that only one or other of these metals is present, it is sufficient to wash and dry the residue, and to fuse it with sodium carbonate and potassium cyanide or with sodium formate in a hollow on charcoal or in a porcelain crucible, by means of the reducing flame of the blowpipe, and to note whether malleable tin or brittle antimony granules are obtained. If, however, several metals may be present, the case is more complicated, since bismuth arsenate also dissolves with difficulty in nitric acid, whilst lead, copper, and other metals may be left in the residue in the form of salts or oxides, together with the antimony oxides and metastannic acid. The best course is to fuse the washed and dried residue for a considerable time with about 4 times its quantity of a mixture of equal parts of sodium carbonate and sulphur in a porcelain crucible *which must be kept well covered*, and then to treat the fused mass, after cooling, with water.

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[1] Alloys of silver and platinum containing very little platinum are soluble, however, in nitric acid.

[2] Very minute quantities of antimony are often completely dissolved

If necessary, and especially when the aqueous extract of the fused mass is of deep yellow colour (which shows that the air was not sufficiently excluded), the fusion of the residue with sodium carbonate and sulphur, and subsequent extraction with water, is repeated and the two solutions united.

If a residue is left it is filtered off, washed, and dissolved in nitric acid. The solution is tested as in Sec. 161, III., (109), for the cations of the fifth and the fourth groups, or the precipitates of the fifth or fourth group obtained from this nitric acid solution are united with the corresponding precipitates from the main nitric acid solution first obtained. The yellow alkaline solution, however, is acidified with hydrochloric acid, whereby sulphides of the sixth group are precipitated, and the precipitate is washed as in Sec. 167 (if necessary after being added to the precipitate of sulphides of the sixth group obtained from the main solution).

45. (*c*) The residue is *white* and *flocculent*. This indicates precipitated *silicic acid*. Since, however, the compounds of the heavy metals mentioned in (*b*) may also be present in this precipitate, a portion of the latter, after thorough washing, is fused on charcoal or in a porcelain crucible with sodium carbonate and potassium cyanide, or with sodium formate, whereby the heavy metals may be detected. If they are found the remainder of the residue is fused with sodium carbonate and sulphur as described in (*b*), and the silicic acid thus obtained in solution. If this solution is acidified with hydrochloric acid, after sufficient *dilution*, filtered from the sulphides of the sixth group (which must be examined as in Sec. 167), and evaporated to dryness, and the residue treated with hydrochloric acid and water, a residue of silicon dioxide will be left (Sec. 115, 3). With regard to the behaviour of the aqueous extract of the fused mass when acidified with hydrochloric acid, see also (104).

(*d*) The residue is *black*. This indicates separated carbon. A small portion is strongly heated for some time on platinum foil to see whether it burns completely. The nature of any residue left is investigated according to (*a*), (*b*), or (*c*).

III. ACTUAL EXAMINATION.

Simple Compounds.[1]

A Substances soluble in water.

Detection of the Cation.[2]

SEC. 157.

General Survey.

In analysing a simple compound to detect the cation present, tests are first made with the group reagents to ascertain to which analytical group it belongs.

Successive tests are therefore applied to determine the behaviour of the aqueous solution towards hydrochloric acid, of the acidified solution towards hydrogen sulphide, the behaviour towards ammonium sulphide (a precipitate with which may consist either of sulphides of the fourth or of hydroxides of the third group), and towards ammonium carbonate and sodium ammonium hydrogen phosphate. If these reactions prove the absence of the members of groups II. to VI. only an alkali ion or ammonium ion can be present. If *one* group reagent has given a positive result there is no need to apply the others, since only *one* cation is present.

Special Process.[3]

1 A small portion of the aqueous not too concentrated solution is **46.** treated with a little hydrochloric acid. If the reaction is alkaline the acid must be added until the liquid shows a decided acid reaction. Effervescence indicates the presence of carbonate ion or sulphide ion, and should be noted for the detection of the anion (68).

(*a*) *No precipitate is formed.* This indicates the absence of **47.** silver and mercurous ions, as also of large amounts of lead ion. The analysis is continued as in (50).

(*b*) *A precipitate is formed.* Hydrochloric acid is added drop by drop until the volume of the precipitate no longer increases, after which an additional 6 to 8 drops are added, and a note taken whether or no the precipitate re-dissolves.[1]

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[1] *Cf.* (3) and Chap. III., Nos. 9 and 10.

[2] In this scheme of analysis attention must also be directed to the anions of arsenites, arsenates, silicates, and cinnamylates, since phenomena may be observed which will enable them to be identified.

[3] With regard to the tabulation of the results, see Appendix III.

If it dissolves the analysis is continued at (50).

If it does not dissolve, and organic substances are present (10), a portion of the liquid in which the precipitate is suspended is shaken with ether. *If the precipitate dissolves* the analysis is continued at (50).[2] *If the precipitate remains insoluble*, or *if organic substances are not present*, the liquid (if necessary separated from the ethereal layer) in which the precipitate is suspended is divided into two parts, and excess of ammonia solution added to *one* of them.

(α) *The precipitate disappears and the liquid becomes clear.* It was silver chloride, and indicates the presence of *silver ion*. As a confirmatory test the original solution is treated with potassium chromate and with hydrogen sulphide (see Sec. 70, 10, 4).

48. (β) *The precipitate becomes black.* It was mercurous chloride, which has been decomposed by the ammonia. This indicates the presence of *mercurous ion*. As a confirmatory test the original solution is treated with stannous chloride and with metallic copper (see Sec. 71, 8 and 9).

49. (γ) *The precipitate remains unaltered.* It is lead chloride, which is not dissolved by ammonia solution. It indicates the presence of *lead ion*. This is confirmed by diluting the other portion of the liquid, in which the precipitate produced by hydrochloric acid is suspended, with a large amount of water, and then heating it. The precipitate, if it really is lead chloride, must dissolve. For further confirmation, portions of the original solution are tested with hydrogen sulphide and with sulphuric acid (See 72, 4 and 11).

50. 2. Hydrogen sulphide water is added to the solution acidified with hydrochloric acid until the liquid has a distinct odour of the gas after being shaken. The liquid is then heated and, after the

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[1] With regard to the formation in exceptional cases of precipitates other than the silver, mercurous, and lead chlorides, see Chap. III., No. 15.

[2] The precipitate, however, is filtered off from the remainder of the solution which has been acidified with hydrochloric acid, dissolved in sodium hydroxide solution, and tested according to Sec. 139, 3, 4, and 7, for cinnamylate ion, care being taken that in the two first reactions the solution is not alkaline. The reaction with ferric chloride will also indicate the presence of benzoate or salicylate ion.

addition of more hydrogen sulphide, is allowed to stand for a time.[1]

(*a*) *The liquid remains clear.*[2] The analysis is continued at (56), or if an acid, not an aqueous solution is in question (Sec. 160), at (84), for lead, bismuth, copper, mercuric, gold, platinum, tin, antimony, arsenic, and ferric ions are not present.

(*b*) *A precipitate is obtained.*

(*α*) *The precipitate is white.* In that case it consists of **51.** separated sulphur, and points to the presence of an oxidising substance which decomposes hydrogen sulphide with the separation of sulphur.[3] Of the cations of this nature ferric ion is the one of most frequent occurrence (Sec. 62, 3). (In this case the colour of the solution changes from yellow to colourless.) The original solution is tested with potassium ferrocyanide (Sec. 62, 8). If iron is not found and if a change of colour in the solution did not indicate the presence of chromate ion or ferricyanogen ion (*cf.* footnote 3), the analysis is continued at (56).

(*β*) *The precipitate is yellow.*[4] It may be the sulphide of **52.** cadmium, arsenic, or tetravalent tin. In order to determine the point, a portion of the liquid in which the precipitate is suspended is treated with ammonia in excess, then with a little ammonium sulphide and heated.

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[1] If a precipitate is immediately formed on the addition of the hydrogen sulphide water, the heating, etc., is unnecessary, but if the liquid remains clear or becomes only slightly turbid, the above process must be strictly followed if the risk of overlooking arsenate ion and stannic ion is not to be incurred.

[2] If the liquid from being dark violet-red in colour becomes colourless with this reagent the presence of permanganate ion is indicated. In this case the scheme for the analysis of mixed compounds is followed (Sec. 170 or 169).

[3] If the colour of the solution changes from reddish-yellow into green, chromate ion is indicated, whilst a gradual change from yellow to pale blue points to the presense of ferricyanide ion. In the former case, two cations are present after the action of the hydrogen sulphide, viz. chromic ion and the cation of the chromate originally in the solution, and the process described in Sec. 170 or 169 should be adopted. In the latter case, the dry substance or the residue obtained by evaporating the aqueous solution is heated with a little concentrated sulphuric acid in a fume cupboard until the greater portion of the sulphuric acid has evaporated, the residue dissolved in water, and the solution, which will now contain the cation originally present in addition to the ferric ion produced from the ferricyanogen ion, is examined as described in Sec. 170.

[4] If the original solution was yellow, it is treated with a larger excess of hydrogen sulphide, and heated to make certain that a white precipitate of sulphur in the yellow solution has not been mistaken for a yellow precipitate.

(*aa*) *The precipitate does not disappear. Cadmium ion* is present, for cadmium sulphide is insoluble in ammonia and ammonium sulphide solutions. Confirmation is obtained by testing the original substance, or the precipitate produced by ammonium carbonate in its solution, by means of the blowpipe (Sec. 77, 10).

(*bb*) *The precipitate disappears.* This indicates *stannic ion* or *arsenic ion*. A portion of the original solution is treated with sodium carbonate.

(*αα*) *A white precipitate is formed.* This indicates *stannic ion*. Confirmation is obtained by reducing this precipitate with potassium cyanide and sodium carbonate, or with sodium formate, before the blowpipe, or in a crucible (Sec. 87 or 88, 17), or by testing the original solution with ammonium nitrate (Sec. 89, 11).

(*ββ*) *No precipitate is formed.* This indicates *arsenic ions*.[1] If the solution contains trivalent arsenic the yellow precipitate was produced immediately by hydrogen sulphide. Confirmatory tests are applied to the original solution as described in Sec 89, 6 and 8. If the solution contains pentavalent arsenic the precipitate was produced by hydrogen sulphide only after heating the liquid, or allowing it to stand for some time. Confirmatory tests are applied according to Sec. 90, 5, 8, and 9.

53. (*γ*) *The precipitate is orange-coloured.* It consists of antimony sulphide, and indicates the presence of *antimony ion*. As a confirmatory test the original solution is treated with zinc in a platinum basin (Sec. 91, 9), and the stage of oxidation in which the antimony is present is determined as in Sec. 92, 13.

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[1] If arsenic ion has been found the solution may still contain a cation. If the original substance was soluble in water this can only be an alkali metal ion. Tests for this are applied to the filtrate from the arsenic sulphide, which has previously been boiled to remove the hydrogen sulphide. If the substance was not soluble in water it is best examined by the method used for mixed compounds. Arsenic may also be present as cation, *e.g.* in arsenic trichloride. Hence, if no other cation has been found, the solution is tested for halogens according to (73).

(δ) *The precipitate is dark brown* It is stannous sulphide, and indicates the presence of divalent *tin*. As a confirmatory test a portion of the original solution is treated with mercuric chloride solution (Sec. 87, 10).[1] **54.**

(ε) *The precipitate is brownish-black or black.* It may be the sulphide of lead, divalent mercury, copper, bismuth, gold, or platinum. To determine the point the following tests are applied to the original solution:— **55.**

(*aa*) Dilute sulphuric acid is added to a portion of the solution A white precipitate indicates *lead ion*. Potassium chromate is used as a confirmatory test (Sec. 72, 12).

(*bb*) A portion of the solution is treated with potassium or sodium hydroxide solution until the reaction is strongly alkaline. A yellow precipitate indicates *mercuric ion*. Stannous chloride or metallic copper is used as a confirmatory test (Sec. 74, 6 and 9).

The presence of mercuric ion may, as a rule, be recognised by the fact that the precipitate, which is formed on the addition of hydrogen sulphide water, does not become black immediately, but only after the addition of excess of the precipitant does it change successively through white, yellow, and orange into black (Sec. 74, 3). In the case of very acid solutions the test with potassium and sodium hydroxide solution is not applicable (Sec. 74, 4).

(*cc*) Excess of ammonia solution is added to another portion. A bluish precipitate, which dissolves to an azure blue solution in excess of ammonia solution, or a blue solution without a precipitate, indicates *cupric ion*. Potassium ferrocyanide is used as a confirmatory test (Sec. 75, 10).

(*dd*) If a white precipitate insoluble in excess of ammonia solution has been obtained in (*cc*), a portion of this precipitate is dissolved on a clock glass in one or two drops of hydrochloric acid diluted with two drops of water, and more water is added to the solution. If a milky turbidity is produced it may be due to bismuthyl chloride, and the presence of *bismuth ion* is indicated.[1] As a confirmatory test a few drops of the original solution are treated with a sodium hydroxide solution of stannous chloride (Sec. 76, 11).

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[1] If a brownish-black precipitate of bismuth sulphide appears to be brown, a mistake may be made here, since in the test with mercuric chloride a white precipitate of bismuthyl chloride may be obtained. If the liquid is rendered strongly acid with hydrochloric acid, this precipitate is not formed, whereas stannous compounds give a precipitate with mercuric chloride, even under these conditions. Moreover, the grey precipitate of metallic mercury, which a solution containing stannous ion gives with mercuric chloride, is not obtained with a bismuth solution.

(*ee*) A portion of the original solution is treated with ferrous sulphate solution. A fine brown metallic precipitate indicates the ions of *gold*. As a confirmatory test the precipitate is heated before the blowpipe, or the original solution is tested with stannous chloride (Sec. 84, 8, *c*).

(*ff*) Ammonium chloride and alcohol are added to a portion of the original solution, concentrated by evaporation if necessary. If a yellow crystalline precipitate is formed the presence of *platinum ion* is indicated. Confirmation is obtained by igniting this precipitate (Sec. 85, 6).

56. 3. A portion of the original solution is treated with ammonium chloride,[2] then with ammonia solution until the reaction is alkaline, and finally (whether or no ammonia produced a precipitate) with a little ammonium sulphide, and gently heated if no precipitate was formed in the cold.

(*a*) *No precipitate is formed.* The analysis is continued at (62), for iron, cobalt, nickel, manganese, zinc, chromium, aluminium, and silicate ions cannot be present.[3]

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[1] If bismuth ion is not found, the white precipitate produced by ammonia indicates mercuric or lead ion, which has escaped detection in (*aa*) or (*bb*), and special tests for which should now be applied.

[2] In order to prevent the ammonia precipitating any magnesium ion that may be present.

[3] This is only conclusive as regards aluminium ion and the ions of many of the heavy metals mentioned, when organic substances, and especially non-volatile organic acids, are not present, since such substances by forming complex ions may influence or prevent the precipitation not only of aluminium and chromic ions but also of manganous ion (*cf.* Sec. 58, 5). If, therefore, the original substance contains organic substances, and the preliminary examination indicates the presence of a metal of the third or fourth group, a portion of the substance should be fused with sodium carbonate and nitrate, the fused mass treated with water, heated with hydrochloric acid, the liquid filtered, and the filtrate tested according to (56) (*cf.* Chap. III, No. 39, 1).

(*b*) *A precipitate is formed.*

(α) *It is black.* This indicates ferrous,[1] nickel, or cobalt **57.** ion. A small part of the original solution is treated with potassium or sodium hydroxide solution.

(*aa*) A dirty greenish-white precipitate is obtained, which soon becomes reddish-brown in the air, and when boiled changes to grey or black. This indicates *ferrous ion.* A confirmatory test is made with potassium ferricyanide (Sec. 61, 10).

(*bb*) A pale green precipitate is obtained, which does not change in colour either in the air or when boiled. This indicates *nickel ion.* A confirmatory test is made with ammonia solution, followed by sodium or potassium hydroxide solution, or with dimethylglyoxine (Sec. 59, 8, 18).

(*cc*) A pale blue precipitate, becoming light red or discoloured and brownish when boiled, indicates *cobalt ion.* A confirmatory test is made by means of borax beads (Sec. 60, 24).

(β) *It is not black.* **58.**

(*aa*) If it is flesh-coloured, it is manganese sulphide, and indicates the presence of *manganous ion.* As a confirmatory test sodium hydroxide is added to the original solution, or the original substance is fused with sodium carbonate, or oxidised to permanganate ion (Sec. 58, 6, 19 and 13).

(*bb*) If it is bluish-green it is *chromic hydroxide.*[2] For confirmation the original solution is treated with sodium hydroxide or the substance is fused into an alkali phosphate bead (Sec. 41, 1 and 13).

(*cc*) If it is white [3] and does not dissolve when heated **59.** with more ammonium sulphide [4] it may be chloride, indicates aluminium ion. As a confirmatory test the washed precipitate is heated with cobaltous nitrate solution before the blowpipe (Sec. 40, 12).

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[1] Ferric ion must have already been detected in (51). If it was overlooked there a red-brown precipitate is produced immediately with sodium hydroxide.

[2] Under certain conditions manganous ion may also be precipitated as green manganous sulphide (Sec. 58, 5).

[3] If the ammonia or ammonium sulphide solutions used contain ammonium carbonate, or the ammonium sulphide solution contains sulphate, any precipitate formed may also be the carbonate or sulphate of an alkali metal In doubtful cases the reagents should be tested with barium chloride and only used if they remain clear (Chap. III., No. 40).

[4] A white precipitate produced by ammonium sulphide and dissolving when heated with excess of the precipitant would be sulphur, which would be precipitated by the action of a substance such as a ferricyanide, capable

62. 4. A portion of the original solution is treated with ammonium chloride, ammonia solution[1] until the reaction is alkaline, and ammonium carbonate, and gently heated.

(*a*) *No precipitate is formed.* This indicates the absence of barium, strontium, or calcium ion. The analysis is continued at (64).

63. (*b*) A precipitate is formed. The presence of barium, strontium, or calcium ion is indicated.

The precipitate is filtered off, washed[2] and dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue heated with a little water, the liquid filtered, and a portion of the filtrate treated with an equal volume of calcium sulphate solution.

(α) *No turbidity is produced, even after 5 to 15 minutes* *Calcium ion* is indicated. As a confirmatory test a portion of the original[3] solution is boiled with a concentrated solution of ammonium sulphate, the liquid filtered, and the filtrate tested with ammonium oxalate (Sec. 36, 3 and 5).

(β) *No turbidity is produced at first, but the solution become turbid after some time. Strontium ion* is indicated A portion of the original solution is treated with hydrochloric acid and evaporated to dryness, and the coloration imparted to a flame by the residue determine (Sec. 35, 10).

(γ) *A precipitate is formed immediately. Barium ion* is indicated. Confirmatory tests with silicohydrofluoric acid or potassium chromate are applied (Sec. 34 6 and 9).

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[1] The liquid must remain clear, otherwise more ammonium chloride mus be added.

[2] If the substance was insoluble in water (Sec. 160, 84, *a*) the precipitat produced by ammonium carbonate is boiled, before the treatment with hydrochloric acid, with excess of sodium carbonate solution, because otherwise thi precipitate might under certain conditions be, not the carbonate, but the borat or an organic salt of an alkaline earth metal.

[3] If the original substance was dissolved, not in water, but in acid (*cf.* 84, *a*) the remainder of the solution which is to be tested with calcium sulphat according to (63) is used instead of the original solution (see footnote 2).

5. The solution tested in (62), in which ammonium carbonate produced no precipitate, is treated with sodium ammonium hydrogen phosphate, a little more ammonia solution added, and the sides of the vessel gently rubbed with a glass rod. **64.**

   (*a*) *No precipitate is formed.* The absence of magnesium ion is indicated. The analysis is continued at (65).

   (*b*) *A crystalline precipitate is formed. Magnesium ion*[1] is indicated.

6. A small portion of the original solution is evaporated in a platinum or porcelain basin, and the residue gently ignited. Should carbonisation occur, owing to the presence of organic substances, the heating is continued at a moderate temperature for some time, the carbonaceous mass extracted with hot water, the liquid filtered, the filtrate evaporated, and the residue gently ignited. **65.**

   (*a*) *No residue is left.* In that case a test is made for *ammonium ion*, by adding calcium hydroxide to the original solution, and noting whether gaseous ammonia is liberated; it may be identified by its odour, by the fumes it produces with acetic acid, and by its reaction on moistened test paper (Sec. 30, 4). **66.**

   (*b*) *A non-volatile residue is left.* This indicates potassium or sodium ion.[2] A portion of the original solution is treated with platinohydrochloric acid or sodium hydrogen tartrate or, if borate ion is present, with perchloric acid (Sec. 28, 4 and 5), the tube well shaken, and its sides rubbed with a glass rod. If the solution has an alkaline reaction it must first be neutralised with hydrochloric acid (if dilute it must be concentrated by evaporation); and if an organic acid is present, the residue obtained in (65) is dissolved in a little water, and the solution divided into two parts, *one* of which is acidified with hydrochloric acid and tested with platinohydrochloric acid.

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[1] The crystalline nature of the precipitate can easily be recognised if it is allowed to stand for some time, and the test-tube then closed and inverted. The small crystals will then be found upon the sides of the tube. A *flocculent* precipitate may be due to aluminium ion, overlooked in (59) or (60).

[2] If an anion of an acid which does not volatilise when heated is present (*e.g.* phosphoric acid, boric acid), or of an acid such as hydroferrocyanic acid, which is decomposed on ignition, but leaves a residue, this conclusion cannot be drawn, since under such conditions even an ammonium salt does not volatilise completely. If there is reason to assume that this is the case, a test is made for ammonium ion as in (66, *a*), and if the result is negative for potassium and sodium ions, as in (66, *b*).

(α) *No precipitate is obtained even after 10 to 15 minutes. Sodium ion* is indicated. As a confirmatory test dipotassium dihydrogen pyroantimonate is added (in the presence of an organic acid, *not* to the *original* concentrated neutral or alkaline solution, but to the second portion of the solution of the residue from the ignition), or the flame coloration is noted (Sec. 29, 3 and 6).

(β) *A yellow or white crystalline precipitate is obtained.* This indicates *potassium ion.* Confirmation is obtained by means of sodium hydrogen tartrate or perchloric acid, or by means of the flame coloration (Sec. 28, 4, 5, and 11).

Simple Compounds.

A. Substances soluble in water.

Detection of the Anion.

1. Inorganic Anions.

SEC. 158.

General Survey

In so far as it is necessary to test for the presence of anions which have not already been detected in testing for the cation, successive tests should be applied by means of the group reagents—*barium chloride* (for sulphate ion), *calcium chloride* (for members of the third division of the first group), and *silver nitrate* (for the second group of anions), and finally by means of separate reactions distinctive of borate ion or of the anions of the third group.

Special process.

It is necessary to consider first of all which anions may accompany the cations which have been detected in the substances soluble in water (*cf.* Appendix IV.), and to bear these in mind in the following scheme of examination, as well as in connection with the results of the preliminary tests.

67. 1. *Arsenite* and *arsenate ion*, and also *silicate ion*, will already have been found in testing for the cation (52), (60).

68. 2. The presence of *carbonate ion*, *sulphide ion*, *chromate ion*, and *ferricyanogen ion* will also have been detected in the above described process of testing for the cation. The two first may be recognised by *effervescing on the addition of hydrochloric acid;* the escaping gases, carbon dioxide and hydrogen sulphide, may readily be distinguished by their odour, whilst, if necessary, the presence of carbon dioxide may be confirmed by means of lime water (Sec. 114, 4 and 5), and that of hydrogen sulphide by means of lead acetate solution (Sec. 124, 4). These reagents may also be used for the detection of free hydrogen sulphide and free carbon dioxide in aqueous solution. The presence of chromate ion and ferricyanogen ion is indicated by the separation of sulphur and change of colour on the addition of hydrogen sulphide water (51, footnote). A solution of a lead or silver salt is used as a confirmatory test for chromate ion (Sec. 101, 8 and 7), and ferrous sulphate to confirm the presence of ferricyanogen ion (Sec. 122, 2).

3. A portion of the aqueous solution (diluted sufficiently with water if concentrated) is acidified with hydrochloric acid, or with nitric acid if silver or mercurous ion has been detected, and treated with barium chloride or nitrate. **69.**
   - (*a*) *The liquid remains clear.* This indicates the absence of sulphate ion. The examination is continued at (70).
   - (*b*) *A finely pulverulent white precipitate is obtained.* This indicates *sulphate ion.* The precipitate must remain insoluble even on the addition of more hydrochloric or nitric acid.[1]

4. Another portion of the solution, which if acid has been rendered neutral or slightly alkaline with ammonia solution, and filtered if necessary, is treated with calcium chloride solution, diluted with 4 to 5 parts of water. **70.**
   - (*a*) *No precipitate is formed.* This indicates the absence of phosphate, oxalate,[2] and fluorine ions, and of any considerable quantity of borate ion. The analysis is continued at (73).

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[1] A *crystalline* white precipitate may be produced by barium chloride or nitrate if the liquid is *strongly* acid and a relatively large amount of the barium salt solution has been added; it dissolves on diluting the liquid with a large quantity of water.

[2] If the cation should be chromic or ferric ion, the non-occurrence of a precipitate on the addition of calcium chloride does not prove that oxalate ion is absent (Sec. 112, end of 4, p. 433). In this case a portion of the original substance should be tested for oxalic acid by means of concentrated sulphuric acid, or sulphuric acid and manganese dioxide (Sec. 110, 9 or 10).

(*b*) *A precipitate is formed.* An excess of acetic acid is *immediately* added.

71. (*a*) *It dissolves readily.* This indicates *phosphate* or *borate ion.* A portion of the original solution, which if acid is rendered slightly alkaline with ammonia, is treated with magnesia mixture (p. 342, footnote 1). A crystalline precipitate indicates the presence of phosphate ion (Sec. 197, 7). A test for borate ion is made as in (76).

72. (*β*) *The precipitate does not dissolve, but the liquid appears milky even after the addition of acetic acid, and the precipitate is pulverulent.* This indicates *oxalate ion.* As a confirmatory test the original substance is treated with manganese dioxide and sulphuric acid (Sec. 110, 10).

(*γ*) *The precipitate dissolves with difficulty and usually incompletely, and the insoluble portion is transparent and flocculent.* This indicates *fluorine ion.* Its presence is confirmed by its etching action on glass (Sec. 111, 6).

73. 5. A fresh portion of the solution is acidified with nitric acid and silver nitrate solution added.

(*a*) *The liquid remains clear.* This proves definitely the absence of chlorine, bromine, iodine, ferro- and ferricyanogen ions, also of thiocyanogen ion and probably of cyanogen ion.[1] The analysis is continued at (76).

(*b*) *A precipitate is formed.*

74. (*a*) *It is orange-coloured.* This indicates *ferricyanogen ion.* As a confirmatory test the original solution is treated with ferrous sulphate (Sec. 122, 2).

(*β*) *It is white or yellowish-white.* The precipitate is treated with excess of ammonia solution, directly when the cation belongs to the first or second group, but after separation and washing when the cation belongs to a higher group.

75. (*aa*) It does not dissolve, even on heating. *Iodine* or *ferrocyanogen ion* is indicated. In the former case the precipitate is pale yellow, in the latter white and gelatinous. The presence of iodine ion is confirmed by means of starch paste or carbon bisulphide and nitrous acid (Sec. 119, 10 or 12), and that of ferrocyanogen ion by means of ferric chloride (Sec. 121, 2).

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[1] Of the soluble cyanides mercuric cyanide in particular is not precipitated; whether this is to be taken into consideration is indicated by the nature of the cation detected; for the method of detecting cyanogen ion in such cyanides, see Sec. 120, 14.

(*bb*) It dissolves with difficulty in the cold, more readily on heating. *Bromine* or *thiocyanogen ion* is indicated. The presence of *bromine ion* is confirmed by testing the original solution with chlorine water (Sec. 118, 6), and that of *thiocyanogen ion* by means of ferric chloride (Sec. 123, 3).

(*cc*) It dissolves readily, even in the cold. *Chlorine* or *cyanogen ion* is indicated. If cyanogen is present, the original substance will usually have had an odour of hydrocyanic acid. As a confirmatory test a solution of a ferrous and ferric salt and sodium hydroxide solution are added to the original solution, and then after a short time the liquid rendered acid with hydrochloric acid (Sec. 120, 7). If a cyanogen ion was not present, the silver precipitate will be due to *chlorine ion*. A portion of the original substance will then yield chlorine when heated with manganese dioxide and sulphuric acid (Sec. 117, 7).

6. To prove the presence of borate ion, or, under certain conditions, to detect small quantities thereof, hydrochloric acid is carefully added to a portion of the original solution until the reaction is distinctly acid, and a strip of turmeric paper partly dipped into the liquid and dried at 100°. If the moistened half of the paper appears brownish-red and when moistened with ammonia solution becomes bluish-black, *boric acid* is present. Confirmation is obtained by the flame coloration (Sec. 109, 6, 7, 8, or 9). **76.**

7. The presence of *nitrate ion* and *chlorate ion* will usually have been indicated by the preliminary examination (5). The presence of the former may be confirmed by means of sulphuric acid and ferrous sulphate (Sec. 130, 6), and that of the latter by testing the solid substance with sulphuric acid (Sec. 131, 7). **77.**

Simple Compounds.

A. Substances soluble in water.

Detection of the Anion.

2. Organic Anions.

SEC. 159.

General Survey.

The detection of organic anions by means of the following scheme presupposes that hydrogen or an alkali metal or ammonium is present as cation. If this is not the case, the cation must be separated. Hence in such cases the preparation of the solution precedes the actual examination.

The examination consists in the use of the group reagents calcium chloride and ferric chloride, followed by special tests for the individual anions.

In the first place it is necessary to consider what anions may occur in association with the cations detected, to form compounds soluble in water (*cf.* Appendix IV.), and in the following tests to have regard to this as well as to the results of the preliminary examination.

Preparation of the Solution.

78. If the substance under examination contains the anion to be detected in the form of an acid or alkali salt, it is suitable for direct examination in accordance with (79), etc., but if another cation is present such cation must first be removed.

In most cases this is effected by boiling the substance or its concentrated aqueous solution with sodium carbonate solution, and filtering off the precipitated carbonate or hydroxide of the cation to be removed. If it is found difficult to separate the cation in this way, it may be precipitated, if it belongs to the fifth or sixth group, by adding hydrogen sulphide to the solution acidified with hydrochloric acid, or, if it belongs to the fourth group, by adding ammonium sulphide to the ammoniacal solution, the precipitate filtered off, the filtrate acidified with hydrochloric acid if the precipitation was effected with ammonium sulphide, and the hydrogen sulphide removed by heating and shaking the liquid (Chap. III., No. 77). Any sulphur precipitated is separated by filtration.

If a cation of the third group is present which cannot be separated by boiling with sodium carbonate (which may be the case with salts of non-volatile organic acids, owing to complex formation), the solution is treated with lead acetate, $(CH_3COO)_2Pb$, the precipitate (the lead salt of the anion to be detected) filtered off, washed and distributed in water, hydrogen sulphide introduced, the lead sulphide filtered off and the excess of hydrogen sulphide removed by heating and shaking the filtrate.

Aluminium ion in such cases may also be precipitated as aluminium silicate by means of sodium silicate (water glass) solution.

If it is a question of detecting acetate or formate ion, acetic or formic acid may be separated from the cation by distillation of their salts with sulphuric acid, and detected in the distillate.

Actual Examination.

Cinnamylate ion will already have been detected, (33, *d*) or (47), footnote 2, p. 570. Hence it need not be taken into consideration here. **79.**

1. A portion of the solution, if alkaline, is acidified with hydrochloric acid until the reaction is acid. (If carbon dioxide is liberated thereby, it must be removed by heating and repeatedly shaking the solution (Chap. III, No. 77). Excessively protracted heating should be avoided to prevent acetic or formic acid being expelled.) The acid or neutral solution is rendered alkaline by the addition of ammonia solution, and then treated with ammonium chloride and calcium chloride in not too small a quantity.
   - (*a*) *No precipitate is formed, even on shaking and allowing the liquid to stand for some time.* This indicates the absence of oxalate and tartrate ions. The analysis is continued at (80).
   - (*b*) *A precipitate is formed.*
     - (α) *It is formed only after some time and is crystalline. Tartrate ion* is indicated. Confirmation is obtained by testing the behaviour of the washed precipitate towards *freshly prepared* sodium hydroxide solution, or by testing the aqueous solution with potassium acetate and acetic acid, or by treating the precipitate produced by calcium chloride with resorcinol and sulphuric acid (Sec. 131, 5 and 17).
     - (β) *It is formed immediately and is finely pulverulent. Oxalate ion* is indicated. Confirmation is obtained by

testing a fresh portion of the aqueous solution, acidified with acetic acid, with calcium sulphate solution (Sec. 110, 7).

80. 2. The liquid from (1, *a*) is treated with about three times its volume of alcohol, and allowed to stand for some hours in a closed flask.

(*a*) *It remains clear.* No citrate, malate, or succinate ions are present. The analysis is continued at (82).

(*b*) *A white precipitate is formed.* This indicates citrate, malate, or succinate ions. The precipitate is filtered off, distributed in a little water and treated with hydrochloric acid, added drop by drop, until solution has just taken place, after which the liquid is heated in a flask with excess of ammonia until it is boiling gently, and then allowed to stand for some time.[1]

(*α*) *The liquid remains clear.* Citrate ion is absent. The analysis is continued at (81).

(*β*) *A heavy white precipitate is formed.* This indicates *citrate ion.* As a confirmatory test the lead salt of the acid is prepared and washed, and its behaviour towards ammonia solution (in which it should dissolve readily) is determined; or better, the barium salt is prepared, and its characteristic microscopical appearance observed, or Stahre's reaction is used (Sec. 136, 6, 5, and 10).

81. 3. A portion of the original solution, or of that prepared according to (78), if not already neutral, is neutralised with ammonia solution or hydrochloric acid, and treated with a little neutral ferric chloride solution. *If a pale brownish-red precipitate is formed*, the presence of *succinate ion* is indicated; *if the liquid remains clear, malate ion* is indicated. As a confirmatory test the lead salt of the acid in question is prepared, and its properties determined (*cf.* Sec. 137, 6, and Sec. 138, 6). The malate ion should also be converted into fumaric acid (p. 509).

82. 4. A portion of the original solution, if not already neutral, is neutralised with ammonia solution or hydrochloric acid, and treated, at first with a very small, and then with a somewhat larger quantity of neutral ferric chloride solution.

(*a*) *A voluminous, flesh-coloured precipitate is formed.* This indicates *benzoate ion.* For confirmation the original substance is tested by Mohler's reaction (Sec. 141, 9).

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[1] Care should be taken that the liquid remains alkaline, and, if necessary, more ammonia should be added.

(*b*) *An intense violet coloration is produced. Salicylate ion* is present.

(*c*) *The liquid assumes a fairly intense deep red colour, and when boiled yields a light reddish-brown precipitate. Acetate* or *formate ion* is indicated.

A portion of the original solid substance, or the residue obtained by evaporating the solution (which, if acid, is first neutralised with sodium hydroxide), is heated with concentrated sulphuric acid and alcohol (Sec. 144, 8). *Acetate ion* may be recognised by the *odour of ethyl acetate.*

Formate ion, the presence of which may be assumed when no acetate ion has been found, is recognised by means of mercuric chloride and silver nitrate (Sec. 143, 6 and 4).

Simple Compounds.

B. Substances insoluble or dissolving with difficulty in hydrochloric or nitric acid or aqua regia.

Detection of the Cation.[1]

SEC. 160.

General Survey.

The detection of the cation of a simple compound in a solution effected by acids follows *essentially the same course as has been described in the case of aqueous solutions* (Sec. 157). A difference occurs, however, in applying the *test with ammonia and ammonium sulphide*, after the absence of members of Groups V. and VI. has been proved, since from acid solutions not only the cations of the fourth group may be precipitated as sulphides, and those of the third group as hydroxides, but there may also be a precipitation of the cations of the second group as phosphates, borates, fluorides, tartrates, and citrates. Hence, on the one hand, if chromic ion has been detected it is necessary to test for phosphate ion, whilst, on the other hand, if a white precipitate is produced by ammonia and ammonium sulphide, it is necessary to consider whether it may be not only zinc sulphide or aluminium hydroxide, but also aluminium phosphate or one of the alkaline earth salts mentioned.

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[1] In this scheme attention is also given to certain salts of the alkaline earth metals, since these are met with at this stage.

It is obvious that further tests for alkaline earth metal ions must be applied to a solution which has given no precipitate with ammonia and ammonium sulphide solution, since they may be present in the original substance in combination with other anions than those mentioned above.

Actual Examination.

83. 1. A portion of the solution in hydrochloric or nitric acid or *aqua regia* is diluted with water,[1] and the solution, if obtained by means of nitric acid, tested for *silver*, *mercurous* and large amounts of *lead ions* by means of *hydrochloric acid*, (46) to (49).

If the solution was effected by means of hydrochloric acid or *aqua regia*,[2] or if no precipitate was produced on adding hydrochloric acid to a nitric acid solution, a portion of the liquid is treated with *hydrogen sulphide water* in large excess, and tested for the cations of the *second division of the fifth group*, for *lead ion*, the cations of the *sixth group*, and for *ferric ion* as in (50) to (55).

If a cation of the fifth or sixth group has not been found, the analysis is continued at (81).

If an ion of a metal which has different valencies has been found, it should be noted that solutions which have been obtained solely by means of hydrochloric acid usually contain the metals in the condition of valency in which they were present before solution, whereas in the case of solutions obtained by means of nitric acid or *aqua regia* there will generally have been a conversion, partial or complete, from lower into higher conditions of valency. Hence, if, for example, an *aqua regia* solution has been prepared, and ferric ion, mercuric ion, stannic ion, or arsenate ion has been detected therein, a special test is required to determine in what condition of valency the metal was originally present, in so far as this question has not been answered already by the behaviour of the substance towards the solvents. In the case of mercury salts, for example, treatment of the solid substance with potassium or sodium hydroxide will often give an immediate decision on the point, since the reagent precipitates yellow mercuric oxide from mercuric salts and black mercurous oxide from mercurous salts, whilst the anions may be easily detected in the filtrate.

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[1] If, on the addition of water, a white turbidity or precipitate is produced, the presence of ions of bismuth or antimony (possibly also of tin) is indicated, *cf.* Sec. 76, 3, and Sec. 91, 4; also Sec. 88, 3. The liquid is heated with hydrochloric acid until the solution again becomes clear, and the analysis then continued at (50). If the original substance dissolves with some difficulty in hydrochloric acid, the precipitate formed on the addition of water may also be lead sulphate, lead chloride, or silver chloride. It then only re-dissolves with very great difficulty. In such cases the original substance should be tested as in Sec. 163.

[2] If the solution also contains chlorine or nitrosyl chloride a separation of sulphur takes place on the addition of hydrogen sulphide, and since this may mask a yellow precipitate of metallic sulphides, *aqua regia solutions should be heated until they no longer smell of chlorine* before adding hydrogen sulphide water (see also Chap. III, No. 19).

2. A portion of the acid solution is freed from carbon dioxide, if **84.** necessary, by heating, and if it only contains a little free acid, is treated with ammonium chloride, and is then rendered alkaline with *ammonia*, and treated with *ammonium sulphide*, whether or no a precipitate was produced by ammonia, and the liquid gently heated.

(*a*) *A precipitate is not produced either by ammonia or by ammonium sulphide.* This indicates the absence of cations of the third and fourth group,[1] and also, if an excessive amount of ammonium salts is not present, the absence of the salts of the alkaline earth metals [2] mentioned in (85). A portion of the acid solution is neutralised with ammonia, and tests for the members of Groups II. and I.[3] are applied as in (62) to (65).

(*b*) *A precipitate is formed.*

(*α*) A *black* precipitate indicates *ferrous*, *nickel*, or *cobalt* ions. They are differentiated as in (57).

(*β*) A *flesh-coloured precipitate* indicates *manganous ion*. Confirmation is obtained as in (58, *aa*).[4]

(*γ*) A *bluish-green* precipitate indicates *chromic ion*, possibly also chromic phosphate [5] A confirmatory test for chromic ion is applied as in (58, *bb*). To determine whether the chromium is present as phosphate, the original hydrochloric acid solution is evaporated with nitric acid nearly to dryness, and tested with ammonium molybdate (Sec. 107, 10).

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[1] It will be seen by footnote 3, p. 574, that this conclusion is only conditionally certain as regards aluminium, chromic (or manganous) ions.

[2] If small quantities of these salts are dissolved in a large amount of hydrochloric acid, they may remain in solution, even on the addition of ammonia, since the resulting ammonium chloride checks the dissociation of the ammonium hydroxide or of the neutral salts of the anions in question. The solubility of borates of the alkaline earth metals is fairly considerable in the presence of ammonium salt, so that even fairly large quantities thereof may not be precipitated by ammonia (*cf* Chap. III, No. 72).

[3] *Cf.* also Chap. III., No. 39.

[4] For the sake of completeness we call attention to the fact that under certain conditions manganous ion may also be precipitated as green manganous sulphide (*cf.* Sec. 58, 5).

[5] *Cf.* also Chap. III, No. 39.

85. (δ) A *white* precipitate may be due to *zinc sulphide*. If it was produced by ammonia alone, it may also consist of *aluminium hydroxide* or *silicic acid*, or of the *phosphate, oxalate, borate, silicate,* or *fluoride* of an *alkaline earth metal,* or of *aluminium phosphate*, since all these are insoluble in water, but are sparingly soluble in hydrochloric acid, and are precipitated when the acid is neutralised (since they are also but slightly soluble in ammonium chloride solution). If organic substances are present, a precipitate produced by ammonia may also be due to a *tartrate* or *citrate* of an *alkaline earth metal*.

To determine which of these substances is present, the following tests are made :—

86. (*aa*) If the behaviour of the substance in the preliminary examination (20) or on solution (33, *c*) pointed to the presence of silicate ion, a portion of the hydrochloric acid solution is evaporated to dryness, the residue moistened with hydrochloric acid, and water added. *Silicic acid*, if present, remains undissolved. The cation in the filtrate is identified according to (56) or (62).

(*bb*) A portion of the original hydrochloric acid solution is treated with a fairly *concentrated solution of potassium or sodium hydroxide* until the reaction is alkaline, and more of the reagent then added to determine whether any precipitate formed is soluble in excess of the alkali hydroxide, and the liquid boiled.

87. (*aa*) *No permanent precipitate is formed.* The presence of *aluminium ion* or *zinc ion* is indicated. The clear alkaline liquid is divided into two portions, and to one of these is added hydrochloric acid until the reaction is acid, and then ammonia solution until it is just alkaline, whilst hydrogen sulphide water[1] is added to the other. A precipitate produced by ammonia, which remains insoluble, even after the addition of more ammonium chloride, indicates *aluminium ion*, but a precipitate produced by a small amount of *hydrogen sulphide water* indicates *zinc ion*. Whether the aluminium was present as phosphate is determined according to (84, *b*, γ).[1]

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[1] See (59, *cc*, 60, *ββ*), footnote 1, p. 576.

($\beta\beta$) *A permanent precipitate is formed.* This indicates the presence of a salt of an alkaline earth metal. The following tests are now applied :—

1. For *phosphate ion* and the alkaline earth metal ion accompanying it, by adding ammonia solution to the hydrochloric acid solution until a precipitate is formed, and then *immediately* adding acetic acid drop by drop (Chap. III., No. 57, *b*) until the precipitate is just re-dissolved, and finally treating the liquid with sodium acetate solution and a drop of ferric chloride solution. The formation of a white precipitate indicates the presence of *phosphate ion*. In that case a little more ferric chloride solution is added until the liquid is distinctly red, after which it is boiled, filtered while boiling hot, and the alkaline earth metal ion, which was originally present as phosphate, is identified in the filtrate (which is now free from phosphate ion), after precipitation with ammonia of any ferric ion still remaining in solution (62) to (64). **88.**
2. *Oxalate ion* is detected by mixing a little of the original substance on a clock-glass with a few drops of water and a little manganese dioxide (free from carbonate), and adding a little concentrated sulphuric acid (Sec. 110, 10). Effervescence indicates the presence of oxalate ion. The cation is identified by igniting a fresh portion of the substance, dissolving the residue in dilute hydrochloric acid, and testing the solution according to (62) to (64).
3. For the detection of *borate ion* the dilute hydrochloric acid solution is tested with turmeric paper (Sec. 109, 5), whilst the cation combined with it is detected by boiling a little of the original substance with water and sodium carbonate, filtering off and washing the precipitated carbonate, and dissolving it in the smallest possible quantity of dilute hydrochloric acid, and treating the solution in the same way as that obtained in (63), or testing it for magnesium ion according to (64). **89.**

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[1] *Cf.* also Chap. III , No. 57, *a*.

4. A test for *fluorine ion* is made by heating a portion of the original substance, or of the precipitate produced in the hydrochloric acid solution by ammonia, with sulphuric acid (Sec. 111, 6). After separation of the fluorine ion, the alkaline earth metal ion now remaining in the residue as sulphate is identified by treating the residue with hydrochloric acid, and testing the solution for calcium ion according to (62), and, if necessary, for magnesium ion according to (64). If neither is found, the residue insoluble in hydrochloric acid is tested according to Sec. 163 for barium or strontium ion.
5. Tests are made for *tartrate* and *citrate ions* (which can only be present if the substance carbonised when ignited in a glass tube), and the cation in combination therewith is detected by boiling the original substance with a solution of sodium carbonate, and filtering the liquid. By this means the alkaline earth carbonate is left on the filter, whilst the anion is obtained in the filtrate. The precipitate is examined according to (63) and the filtrate according to (79).

Simple Compounds.

B. Substances insoluble or dissolving with difficulty in water, but soluble in acids.

Detection of the Anion.

1. Inorganic Anions.

Sec. 161.

General Survey.

In this case it is advisable to take into consideration, from the results of the solubility tests and the preliminary examination, what anions may be associated with the cations detected, and then to apply tests for the individual anions in the following order:—

Process in detail.

90. 1. *Chlorate ion* cannot be present, for all the chlorates are soluble in water. *Nitrate ion*, which may be present in the form of a basic salt, will already have been detected by ignition in a glass tube (8, *cc*), as will also *cyanogen ion* (8, *gg*). The latter will also usually have been identified in the course of solution (33, *g*). With regard to cyanogen compounds insoluble in water, see

Sec. 180. The presence of *silicate ion* will have been indicated in the test with alkali phosphate (20), or in the course of solution (33, *c*). As a confirmatory test the hydrochloric acid solution is evaporated to dryness and the residue treated with hydrochloric acid and water (Sec. 115, 3).

2. *Arsenite* and *arsenate ion*,[1] *carbonate ion*, *chromate ion*, and *sulphide* **91.** *ion* will already have been detected in the preliminary examination, in the course of solution, or in testing for cations. Thus the presence of chromate ion will have been indicated by the red or yellow colour of the compound, by the evolution of chlorine on boiling with hydrochloric acid (33, *c*), and by the subsequent detection of chromic ion in the solution. Confirmation is obtained by fusing the substance with sodium carbonate (Sec. 101, 11).

3. A portion of the substance is boiled with nitric acid.
   (*a*) If nitric oxide gas is evolved and sulphur separates, the **92.** presence of a *sulphide* is confirmed.
   (*b*) If violet vapours are evolved, the compound is an iodide.[2]
   (*c*) If reddish-brown vapours with an odour resembling that of chlorine are produced, the presence of a bromide may be inferred.[2] In this case the vapours impart a yellow coloration to moist starch (Sec. 118, 8).

4. A portion of the nitric acid solution, previously filtered if any **93.** insoluble residue has been left after the treatment with nitric acid, is diluted, and treated with silver nitrate. A white precipitate, soluble after washing in ammonia solution and melting without decomposition when heated, indicates *chlorine ion*.[2]

5. A portion of the substance is boiled with hydrochloric acid, the **94.** solution filtered, if necessary, diluted with water, and treated with barium chloride. If a white precipitate is formed, which does not disappear on the addition of a large amount of water, a *sulphate* is present.

6. Tests for *borate ion* are applied as in Sec. 109, 5, 7, 8, or 9. **95.**

7. If none of the anions mentioned above has been found, there is reason for concluding that *phosphate*, *oxalate*, or *fluorine ion* is present, or that an anion is absent. The presence of oxalate

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[1] Hydrogen sulphide is the best reagent for distinguishing between arsenite and arsenate ions in compounds which are insoluble in water, but dissolve in hydrochloric acid.

[2] Sometimes, especially in the case of mercurous iodide, bromide, or chloride, the halogen ions may be detected more readily by boiling the substance with potassium or sodium hydroxide solution, and testing the filtrate according to (73).

ion will usually have been indicated in the preliminary examination (8, *ee*). Since phosphate ion will already have been detected if it was in combination with an alkaline earth metal, aluminium, or chromic ion; fluorine ion if in combination with an alkaline earth metal ion; and oxalate ion when combined with barium, strontium, or calcium ion (84) to (89), it is only necessary to test for these cations when another cation has been found. For this purpose the cation is precipitated by boiling the acid solution with excess of sodium carbonate, and the liquid filtered. If this does not effect the end in view, the cation should be precipitated with hydrogen sulphide if it belongs to Groups V. or VI., or with ammonium sulphide if it belongs to Group IV., and the liquid filtered. If the cation has been precipitated with ammonium sulphide, the filtrate is acidified with hydrochloric acid, and, whichever precipitant was used, the liquid is boiled to expel hydrogen sulphide, and, if necessary, filtered. A portion of this solution is tested for oxalate and phosphate ions according to (70) and (72), after acidification with hydrochloric acid, and boiling to remove carbon dioxide if it contains sodium carbonate, whilst fluorine ion is detected by treating the liquid with calcium chloride and ammonia solution, and testing the separated and washed precipitate according to Sec. 111, 6. If the cation was aluminium, chromic, or magnesium ion, a test for phosphate ion is applied according to Sec. 107, 10; for oxalate ion by means of manganese dioxide and sulphuric acid (Sec. 110, 9); and for fluorine ion by means of sulphuric acid (Sec. 111, 6).

Simple Compounds.

B. Substances insoluble or dissolving with difficulty in water, but soluble in acids.

Detection of the Anion.

2. Organic Anions.

SEC. 162.

General Survey.

In this case the examination follows essentially the same course as that of substances soluble in water after the anion has been dissolved as a sodium salt by boiling the substance with sodium carbonate solution, or after the cation has been separated and an aqueous solution obtained by another method. Only in the case of certain tests is an indication given beforehand by the results of the solubility test, the preliminary examination, and the examination for cations, as to what anions may possibly be present.

Process in detail.

1. *Formate ion* cannot be present, since its salts are all soluble in water. **96.**
2. *Acetate ion* will already have been easily recognised in the preliminary examination by the evolution of acetic acid or acetone on heating the substance in a glass tube (10). Confirmation is obtained by means of sulphuric acid and alcohol (Sec. 111, 8).
3. *Cinnamylate ion*, and, as a rule, also *benzoate ion* and *salicylate ion*, may be recognised at once by the fact that the acids separate in crystalline form on dissolving the substance in hydrochloric acid, or on cooling the hydrochloric acid solution. As confirmatory tests the precipitate is filtered off, washed with a little water, and dissolved in water containing a little ammonia, and the *neutral* solution treated with ferric chloride solution (Secs. 139, 4; 141, 3; and 142, 7). To determine whether cinnamylate ion or succinate ion is present, a test is made with calcium chloride and with manganous chloride (Sec. 139, 5 and 3).
4. A portion of the substance is boiled for a considerable time with excess of sodium carbonate solution, and the liquid filtered while hot. In most cases any organic acid present will be contained in the filtrate as a sodium salt. The filtrate is slightly acidified with hydrochloric acid, the carbon dioxide expelled by heat, and the liquid then tested as described above (Sec. 159). In the presence of cations of Group IV., and also of lead ion, this method does not effect complete separation. In such exceptional cases ammonium sulphide is added to the filtrate, after the boiling with sodium carbonate, until the cation is precipitated, and the liquid again filtered and tested as described in (78). **97.**

Simple Compounds.

C. Substances insoluble or dissolving with difficulty in hydrochloric acid, nitric acid, and aqua regia.[1]

Detection of Cation and Anion.

SEC. 163.

General Survey.

Insoluble substances may be classified into three sub-divisions: insoluble elements, lead and silver compounds, and the compounds of the earths and alkaline earths, to which may also be added silicon dioxide and stannic oxide.

The members of the first group, *carbon* and *sulphur*, may be recognised by their appearance, or will have been detected already in the preliminary examination, so that they need only be identified. This also applies to chromic oxide.

The two other groups are differentiated by their behaviour on treatment with ammonium sulphide. Lead and silver compounds turn black, whilst the others remain white.

If a substance belonging to the second or third sub-division is present, and its nature has not been ascertained by means of special reactions, it is decomposed by fusion with potassium and sodium carbonates in a porcelain or platinum crucible, and the residue treated with water. The anion is then detected in the solution, and the cation in the residue insoluble in water.

Process in detail.

98. The only substances of frequent occurrence which have to be taken into consideration in the following pages are *barium, strontium,* and *calcium sulphates, calcium fluoride, silicon dioxide, aluminium oxide,* either strongly ignited or of natural occurrence, *lead sulphate, chloride,* and *bromide, silver chloride, bromide, iodide,* and *cyanide, stannic oxide* (ignited and of natural occurrence), ignited *chromic oxide,* and lastly *sulphur* and *carbon.* With regard to simple silicates, reference may be made to Sec. 181, and with regard to ferro- and ferricyanides to Sec. 180. The preliminary examination, and often also the behaviour on treatment with solvents (8, *gg*), (20), (33, *c* and *g*), will indicate whether such substances have to be taken into consideration.

---

[1] If organic acids are present, the substance insoluble in acids may be cinnamic acid. With regard to its identification, see (33, *d*).

Calcium sulphate and lead chloride are not insoluble in water; lead sulphate (and silver chloride) may be dissolved in a large amount of hydrochloric acid. These compounds, however, are so sparingly soluble that they are seldom completely dissolved, and they are, therefore, again dealt with, so that, if by chance they have escaped detection in the examination of the aqueous or acid solution, they may be found at this stage.

1. Free *sulphur* must already have been recognised in the preliminary examination (9, *aa*) or (11).
2. *Carbon* is usually black, and is insoluble in *aqua regia*; it burns[1] on platinum foil which is heated from beneath, and when fused with potassium nitrate yields potassium carbonate.
3. *Chromic oxide* is green or blackish-green, and must already have been recognised in the bead test with alkali phosphate in (18).
4. Ammonium sulphide is poured over a small quantity of the substance. **99.**
    (*a*) *The substance becomes black.*[2] This indicates the presence of a lead or silver salt.
    - (α) *It melts without decomposition in a small tube* (3). This indicates lead chloride or bromide, or silver chloride, bromide, or iodide. One part of the compound is fused with four parts of sodium and potassium carbonates in a small porcelain crucible, the mass cooled and boiled with water, the extract filtered, and the filtrate tested for *chlorine, bromine*, and *iodine ion* according to (73), whilst the residue, which is either metallic *silver* or *lead oxide*, is dissolved in nitric acid, and the solution tested according to (46).
    - (β) *When heated in a glass tube it evolves cyanogen, and leaves a residue of metallic silver.* The presence of *silver cyanide* is proved.
    - (γ) *It does not change when ignited in a glass tube.* It is *lead sulphate*. A portion of the substance is boiled with a solution of sodium carbonate, the liquid filtered, and the filtrate acidified with hydrochloric acid, and tested for *sulphate ion* with barium chloride, whilst the residue is washed and dissolved in nitric acid, and

---

[1] Graphite can only be completely burned when strongly heated in a current of oxygen.

[2] A slight darkening, due to the presence of an impurity, usually a small amount of an iron compound, is not to be regarded as blackening, and is to be ignored.

the solution tested for *lead ion* by means of hydrogen sulphide and sulphuric acid (Sec. 72, 4 and 11).

100. (*b*) *The substance remains white.* This indicates the absence of a lead or silver salt.

(*α*) A portion of the substance is tested for *stannic oxide* by heating it in the *lower* reducing flame with a borax bead coloured slightly blue with cupric oxide (Sec. 87, 18). If the bead becomes reddish-brown or ruby-red, a confirmatory test for the presence of stannic oxide is made by reducing a little of the substance with sodium carbonate and potassium cyanide, or with sodium formate (Sec. 87, 17).

(*β*) A small portion is intimately mixed with finely ground quartz powder, and the mixture moistened with a few drops of concentrated sulphuric acid in a small crucible, which is then *gently* heated on an iron plate or a small sand bath. (Direct heating with a burner may easily lead to erroneous conclusions.)

(*aa*) *White fumes of silicon fluoride are developed, which redden moistened litmus paper*[1] *and produce a turbidity, due to separated silicic acid, in a drop of ammonia solution held over the crucible.* This indicates *calcium fluoride.* A little of the finely ground substance is decomposed with sulphuric acid in a platinum crucible, and the presence of fluorine ion confirmed by its etching action on glass (Sec. 111, 6). The residue is boiled with hydrochloric acid, the solution filtered, and the filtrate neutralised with ammonia, and tested for *calcium ion* by means of ammonium oxalate.

(*bb*) *Fumes which redden litmus paper, and produce a turbidity in a drop of ammonia solution suspended over them, are not developed.* A small portion of the very finely ground substance is mixed with four times its quantity of sodium and potassium carbonates, and the mixture fused in a platinum crucible. The fused mass is boiled with water, and the liquid filtered from any residue, *which is*

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[1] An acid reaction by itself is no proof of the presence of calcium fluoride, since it may be due to sulphuric acid, if the mixture has been heated somewhat too strongly

then washed. The filtrate is acidified with hydrochloric acid, and divided into two portions, one of which is tested for *sulphate ion* with barium chloride, and the other (if sulphate ion is not present) for *silicate ion* by evaporating the acidified liquid (Sec. 115, 3). If no silicate ion is found, the residue from the evaporation is dissolved in hydrochloric acid, and tested for *aluminium ion* by means of ammonia solution.

If pure *silicon dioxide* was present, the mass obtained by fusion with sodium and potassium carbonates must have dissolved to form a clear solution, but if silicates were also present, their cations will have been left as insoluble oxides or carbonates, and may be further examined, see Sec. 181. In the presence of *aluminium oxide*, a clear solution of the fused mass in water is only to be expected, when a large amount of sodium and potassium carbonates have been used at a high temperature.

If sulphate ion was found, the carbonate of the alkaline earth metal present will remain on the filter. It should be *thoroughly washed* and dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue treated with water, and the chloride solution tested for *barium*, *strontium*, and *calcium ions* in the same way as that obtained in (63).

Mixed Compounds.[1]

A. Substances soluble and insoluble in water, but soluble in hydrochloric acid, nitric acid, or aqua regia

Detection of Cations.

General Survey.

The systematic course described in the following pages for the detection of cations in *one* solution depends upon the use of a number of group reagents to detect the presence of different analytical groups, and in the complete separation of these groups (if present) in the form of precipitates.

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[1] This expression is used here and in the following pages to indicate mixtures and compounds in which all the cations and anions of frequent occurrence may be present.

The individual members of a group are then separated from one another according to the methods of separation given in the second chapter of the first part of this book in the "Summary and Remarks," at the end of the description of the reactions of the cations of a group (Secs. 31, 38, 42, 55, 63, 73, 78, 86, 92).

The group reagents used are *hydrochloric acid*, *hydrogen sulphide*, *ammonium sulphide* (or sodium sulphide), *ammonium carbonate* (and sodium ammonium hydrogen phosphate).

The same method is invariably followed for the separation of the different groups, a group reagent being added so long as it produces a precipitate: this is filtered off and washed, and the next group reagent added to the filtrate.

The following scheme is based on this method :—

(*a*) *Hydrochloric acid* precipitates the members of the first division of the fifth group, *silver and mercurous ions* being *completely* precipitated, but *lead ion incompletely*, because the chlorides of the two first mentioned cations are practically insoluble, that of lead ion sparingly soluble, and the chlorides of all the other cations soluble in water.[1] (For the separation of these substances from one another, see Sec. 164.)

(*b*) *Hydrogen sulphide*, when introduced into a solution which has been acidified with hydrochloric acid, and from which any precipitate produced thereby has been filtered off, precipitates any members of the *sixth group* or of the *second division of the fifth group* (including lead ion) which may be present, because the sulphides of these elements are insoluble in acids, whereas those of the members of Groups I. to IV. are soluble therein.

(*c*) The sulphides of the *sixth* and *fifth* groups may be separated from one another by treatment with *ammonium* (or *sodium*) *sulphide solution*, because the members of the sixth group are soluble therein, through the formation of sulpho salts, whereas the sulphides of the cations of the fifth group are not dissolved.

The precipitate produced by hydrogen sulphide is, therefore, filtered off, and treated with *alkali sulphide solution*, and in case it does not dissolve completely, the insoluble sulphides of the fifth group (second division) are filtered off, whilst the sulphides of the sixth group are re-precipitated by acidifying the filtrate with hydrochloric acid.

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[1] The somewhat complicated relationships which arise when an *alkaline* solution is present are not taken into consideration here. For further details on this point, see (101) and (104).

The separation of the individual members of the sixth group is effected as described in Sec. 167, whilst those of the second division of the sixth group are separated as in Sec. 168.

(*d*) The liquid in which neither hydrochloric acid nor hydrogen sulphide has produced a precipitate, or the filtrate from precipitates produced by those reagents, will now contain only the members of Groups I. to IV. It is rendered alkaline with ammonia, and treated with *ammonium sulphide*. (Organic substances which, if present, might prevent the precipitation of members of the third group, are destroyed before the addition of ammonia and ammonium sulphide, by evaporating the solution to dryness, fusing the residue with alkali carbonate, and treating the fused mass first with water and then with hydrochloric acid.)

By this means the cations of the *fourth group* are precipitated as *sulphides*. There is also a simultaneous precipitation (even on neutralising the liquid with ammonia) of the members of the *third group* as *hydroxides* or phosphates; and if certain anions (phosphate, oxalate, fluorine, borate, silicate, tartrate, or citrate ions) are present, the members of the second group are also precipitated more or less completely as salts of these, since all the compounds mentioned are practically insoluble in water. They may be separated as in Sec. 170. The solution will then contain only the members of Group I. and also, in so far as they are not precipitated as phosphates, etc., by ammonia, the members of Group II. In order, in the case of the latter, to prevent the precipitation of magnesium ion (as hydroxide, which, however, would only be incomplete), the dissociation of the ammonium hydroxide must be checked by the presence of a sufficient quantity of an ammonium salt (*cf.* Sec. 5, p. 31). If necessary, therefore, a corresponding amount of ammonium chloride must be added prior to the ammonia solution.

(*e*) The solution in which the above-mentioned group reagents have produced no precipitate, or the filtrate from precipitates produced by them, is treated with *ammonium carbonate*.

This precipitates *barium, strontium,* and *calcium ions* as carbonates. These are separated as described in Sec. 171, whilst magnesium ion and the members of the first group remain in solution. Acid solutions are first treated with ammonia until alkaline, since otherwise carbon dioxide would be liberated, and might form soluble hydrogen carbonates of barium, strontium, and calcium. In order to prevent a precipitation of magnesium ion, care must be taken that a sufficient quantity of a neutral ammonium salt is present, as in the case of (*d*).

(*f*) The solution, which may still possibly contain alkali metal ions or magnesium ion, is tested for the *latter* by adding to a *portion* of it ammonia and ammonium chloride, if it is not already ammoniacal in (*d*) or (*e*), and then *sodium ammonium hydrogen phosphate*. The characteristic crystalline precipitate of *magnesium ammonium phosphate* is not suitable, however, for the separation of magnesium, because the presence of phosphate ion would make the tests for alkalis in the filtrate more difficult (and if sodium phosphate had been used for the precipitation the presence of added sodium would render them impossible).

The separation of magnesium ion is effected, when required, by means of barium or calcium hydroxide, the excess of which is removed from the filtrate by means of ammonium carbonate. For details of the method of removing disturbing substances from the solution before applying the tests for alkali metals, and for the detection of the individual metals, see Sec. 173.

(*g*) The test for *ammonium ion* is made upon the original solution, since it is necessary to add *ammonium compounds* to the solution in separating the metals of Groups II. to IV.

The separation of the various cations in a solution in the form of precipitates belonging to different groups, and their further separation into individuals, may be represented in the form of a table as follows :—

Separation of Cations into Groups.

<table>
<tr><td colspan="7">In Solution Groups I. to VI.</td></tr>
<tr><td colspan="5">(<i>a</i>) + HCl.</td><td colspan="2">(<i>g</i>) + Ca(OH).
Evolution of Gas. NH_4.</td></tr>
<tr><td rowspan="5">Precipitate V_1.
Ag, Hg^I, Pb (incomplete) as Chlorides. For separation, see Sec. 161.</td><td colspan="6">Filtrate : I. to IV, V_2 (including remainder of Pb), VI.
(<i>b</i>) + H_2S.</td></tr>
<tr><td colspan="2">Precipitate : VI. V_2. (including remainder of Pb) as sulphides.
(<i>c</i>) + $(NH_4)_2S$.</td><td colspan="4">Filtrate : I. to IV.
(<i>d</i>) + $(NH_4)_2S$.</td></tr>
<tr><td rowspan="3">Solution VI + HCl, Precipitate. VI. as sulphides. For separation see Sec. 167.</td><td rowspan="3">Residue : V_2, (including remainder of Pb) as sulphides. For separation, see Sec. 168</td><td rowspan="3">Precipitate : IV. as sulphides, III. as hydroxides, (II. as salts only in presence of corresponding anions) For separation, see Sec. 170.</td><td colspan="3">Filtrate : I. and II.
(<i>e</i>) + $(NH_4)_2CO_3$.</td></tr>
<tr><td rowspan="2">Precipitate Ca, Sr, Ba as Carbonates For separation, see Sec. 171.</td><td colspan="2">Filtrate : Mg. Test for Mg with $NaNH_4HPO_4$; if positive.
(<i>f</i>) + $Ba(OH)_2$.</td></tr>
<tr><td>Precipitate : Mg as hydroxide.</td><td>Filtrate : I. Detection of K and Na. See Sec. 173.</td></tr>
</table>

SEC. 164.

Treatment with Hydrochloric Acid.

Detection of silver ion, mercurous ion (lead ion).

The systematic course for the detection of cations is essentially **101.** the same, whether the substance under examination is soluble in water, or whether the aqueous solution has a neutral, acid, or alkaline reaction, for the reason that in all cases in which solution has not been effected by hydrochloric acid or *aqua regia* an addition of hydrochloric acid is made.

Different phenomena may occur, however, on this addition, according to whether an aqueous, nitric acid, or alkaline solution is present.

(A difference is also to be observed between the behaviour of pure aqueous and acid solutions in the separation of the precipitate produced by ammonium sulphide. See Sec. 170.)

In the case of alkaline solutions a series of other substances (silicon dioxide, sulphides) may be precipitated, in addition to the cations of Group V_1. With regard to the procedure in this case, details are given in (104) to (108).

The following course of treatment is applicable to any precipitate produced in *aqueous* or *nitric acid solutions* (solutions obtained by means of hydrochloric acid or *aqua regia* obviously need not be considered here).

General Survey.

The solution is treated with hydrochloric acid and filtered from any precipitate produced.

The precipitate produced by hydrochloric acid may contain the chlorides of silver, mercurous and lead ions. (With regard to other substances simultaneously precipitated, see (102, *b*), (103, small type), and Chap. III., No. 15.) The two first are not soluble in hot water, whereas lead sulphide is soluble therein. Silver and mercurous chlorides may be differentiated by their behaviour towards ammonia solution. The former is soluble in that solvent, and may be reprecipitated from its solution by means of nitric acid, whereas the latter remains insoluble, but is converted into a black mixture of metallic mercury and mercuric ammonium chloride. This may be represented in tabular form as follows :—

Separation of First Division of Group V.

<table>
<tr><td colspan="3">These may be present in the precipitate produced by HCl·
$AgCl$, Hg_2Cl_2, $PbCl_2$.
On treatment with hot water—</td></tr>
<tr><td colspan="2">Insoluble residue: $AgCl$, Hg_2Cl_2; treated with NH_4OH.</td><td rowspan="2">Dissolved: $PbCl_2$
H_2S precipitates black $PbCl_2$
H_2SO_4 precipitates white $PbSO_4$.</td></tr>
<tr><td>Insoluble black residue:
$Hg + Hg(NH_2)Cl$</td><td>Dissolved:
$Ag(NH_3)_2Cl$
HNO_3 precipitates $AgCl$</td></tr>
</table>

Process in detail.

102. I. A pure aqueous solution is present.

A portion of the solution prepared for the detection of the cation is treated with a little hydrochloric acid.

1. *The original solution was acid or neutral.*

   (*a*) *No precipitate is formed.* The absence of silver or mercurous ion is indicated. The analysis is continued at Sec. 165.

   (*b*) *A precipitate is formed.* More hydrochloric acid is added, drop by drop, until the volume of the precipitate no longer increases, after which an additional six to eight drops are added, the liquid shaken, and a note made as to whether a precipitate insoluble even in excess of hydrochloric acid is left. If this is the case, and if organic substances are present (*cf.* 10), the solution with the precipitate in suspension is shaken with ether.

   (*α*) *The precipitate dissolves completely.* Silver and mercurous ions are not present. The precipitate consisted of organic acids. Tests for these are made as in (184), and the examination continued at (103).

   (*β*) *A residue insoluble in ether is left.* It is silver, mercurous, or lead ion.

   To determine whether organic acids were also precipitated, the ethereal layer is separated from the aqueous solution (Chap. III., No. 78), and cautiously evaporated, so that the ether does not take fire.

   (*αα*) *No residue is left.* This shows the absence of organic acids in the precipitate produced by hydrochloric acid. The analysis is continued at (103).

(*bb*) *A residue is left.* The presence of cinnamic, benzoic, or salicylic acid is indicated. The analysis is continued at (103).

The whole of the solution intended for the detection of the cation is treated with a corresponding quantity of hydrochloric acid, shaken, and filtered. **103.**

Since any antimonyl chloride or bismuthyl chloride which may be precipitated at first re-dissolves in excess of hydrochloric acid, the permanent precipitate of cations produced by hydrochloric acid can only contain silver, mercurous, or lead ions as chlorides (see Chap. III., No. 15).

The precipitate left on the filter is washed twice with cold water, and the filtrate and washings further examined according to Sec. 165.

Any turbidity produced when the filtrate and washings are mixed may be ignored (see Chap. III., No. 15).

The precipitate left on the filter, if it does not consist solely of organic acids (102, *b*, *α*), is then treated as follows :—

(*α*) *If it contains organic acids* in addition to the chlorides of Group V$_1$ (102, *b*, *β*, *bb*), it is washed off the filter by means of a jet, and distributed in water, the latter shaken in a small cylinder with ether, and the ethereal layer separated from the aqueous layer (Chap. III., No. 78). The ethereal layer is tested for organic acids as in (181), and the aqueous layer heated (carefully until the ether has been evaporated), and filtered if any insoluble deposit is left. The solution in hot water is tested as in (*β*) with hydrogen sulphide and sulphuric acid, and any residue tested for silver and mercurous ions as in (*γ*) and (*δ*).

(*β*) *If the precipitate produced by hydrochloric acid does not contain an organic acid*, it is washed with hot water on the filter, and the filtrate tested for *lead ion* by means of *hydrogen sulphide*, and also by means of *sulphuric acid*.

If no precipitate has been formed, it only shows that no lead ion was present in the precipitate produced by hydrochloric acid, but not that lead ion is altogether absent, since in fact dilute solutions of lead salts do not give a precipitate with hydrochloric acid.

If the precipitate produced by hydrochloric acid *contains* lead chloride, it should be treated repeatedly with boiling water, so as to dissolve the lead chloride as completely as possible.

(γ) *If a precipitate has been left on the filter,* it is treated with *ammonia solution.* If it becomes grey or black, *mercurous ion* is present.

(δ) *The ammoniacal washings from* (γ) *are treated with nitric acid until the reaction is strongly acid.* (If a precipitate is formed, it is tested to see whether it remains insoluble when shaken with ether, in case organic acids should be present.) If a white caseous precipitate (insoluble in ether) is obtained, or an opalescence in the case of minute quantities, *silver ion* is present.

If the precipitate still contains lead chloride, the ammoniacal solution will generally appear turbid, owing to the detection of basic lead salt. This has no influence on the separation of silver ion, since the basic lead salt dissolves on the addition of nitric acid.

104. 2. *The aqueous solution has an alkaline reaction.*

(*a*) *No evolution of gas takes place on the addition of hydrochloric acid, and no precipitate is formed, or, if formed, re-dissolves on the addition of more acid.* The analysis is continued at Sec. 165.

105. (*b*) *The addition of hydrochloric acid causes an evolution of gas—hydrogen sulphide, hydrocyanic acid, carbon dioxide.* This indicates respectively *sulphides, cyanides,* or *carbonates.* If, at the same time, a precipitate is formed, it is examined as in (*c*). The nature of the gas is indicated by its odour.

(α) *The escaping gas has an odour of hydrogen sulphide.* As a confirmatory test, the gas is tested with paper impregnated with an alkaline lead solution: A brown coloration points to the presence of *monosulphides of the alkali metals,* or of *hydrogen sulphides of the alkali or alkaline earth metals.* If no precipitate was produced by hydrochloric acid, the acidified solution is tested as in Sec. 170 or 169; otherwise as in (*c*, β, or γ), (107), or (108).

(β) *The escaping gas has the barely perceptible odour of carbon dioxide.* If no precipitate was produced by hydrochloric acid, the analysis is continued at Sec. 165; otherwise at (*c*).

(γ) *The escaping gas has an odour of hydrogen cyanide.* Confirmation is obtained as in Sec. 154 (whether or no hydrogen sulphide or carbon dioxide was also evolved). The presence of cyanides of alkali metals is indicated. If a precipitate was produced by hydrochloric acid, the analysis is continued at (*c*, γ) (108); otherwise the liquid is boiled (in a fume cupboard) until all hydrocyanic acid has been expelled, and the analysis continued at Sec. 165, or, if hydrogen sulphide is also absent, at (170) or (169).

If it is not possible to decide whether there is an odour of hydrogen cyanide in addition to that of hydrogen sulphide, a fresh portion of the solution is treated with potassium dichromate and then with hydrochloric acid, and the odour again noted.

(*c*) *On the addition of hydrochloric acid a precipitate is formed, which does not dissolve in excess of the acid, even when boiled.*[1] **106.**

(*a*) *Neither hydrogen sulphide nor hydrogen cyanide is evolved.* The liquid is filtered,[2] the precipitate washed, and the united filtrate and washings tested according to Sec. 165.

(*aa*) *The precipitate is white.* It may be a lead or silver salt, which is insoluble or only sparingly soluble in water (*lead sulphate* or *chloride*, *silver chloride*, etc.), or also *silicic acid*. It is tested for the cations and anions of the inorganic compounds present according to Sec. 179, having regard to the possibility that any chloride of lead or silver detected may have been formed in the course of the examination itself.[3] **107.**

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[1] If organic substances are present, a test is made to determine the insolubility in ether of any precipitate produced. Only when it is insoluble are the directions in (106) and (107) applicable. Should there be a possibility of the precipitates there mentioned containing any cinnamic, benzoic, or salicylic acid, these substances may be extracted with ether before continuing the examination.

[2] If there is reason to suppose that the precipitate contains silicic acid, which, as a rule, may be recognised by its gelatinous character, it is advisable to evaporate it with hydrochloric acid, as described in Sec. 182 (221), so as to obtain an insoluble residue of silicon dioxide, and again to treat this residue with hydrochloric acid and water before filtering off the precipitate.

[3] If organic acids have been detected in the preliminary examination

(*bb*) *The precipitate is yellow or orange.* It may be *arsenic sulphide*, if it has not been boiled for a long time, or only with dilute hydrochloric acid ; or it may be *antimony sulphide* or *stannic sulphide*, which was dissolved by ammonia, potassium hydroxide, sodium hydroxide, or sodium phosphate solutions, or by any other alkaline liquid, with the exception of alkali sulphide or cyanide solutions. The precipitate, which may also contain silicic acid, is treated according to (40).

(β) *Hydrogen sulphide is evolved, but not hydrogen cyanide.*[1]

(*aa*) *The precipitate is a pure white deposit of sulphur*[2] (which is completely soluble when vigorously shaken with benzene or petroleum spirit Chap. III., No. 27). In that case an *alkali polysulphide* is usually present. The presence of such a compound may also be recognised by the fact that the alkaline solution appears yellow or brown, and that on the addition of acid an odour of hydrogen polysulphide may be detected as well as that of hydrogen sulphide. The liquid is boiled, filtered, and the filtrate treated as in Sec. 170 or 169, and the precipitate[2] as in Sec. 179.[3]

(*bb*) *The precipitate is coloured* (or was not completely soluble in benzene or petroleum spirit). In that case the presence of a *sulpho salt* (of a member of Group VI.) may be inferred. The precipitate would thus be a sulphide of *gold, platinum, tin, antimony,* or *arsenic*. It might also, however, consist of or contain *mercuric sulphide* or *cupric* or *nickel sulphide* (since the first-mentioned is

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(10, *h*, *i*), the precipitate may also be or contain *cinnamic, benzoic,* or *salicylic acid*. A test for these is made by means of ether as described in (102) and (103), and these anions identified according to Sec. 176 (184).

[1] With regard to determining whether hydrogen cyanide is liberated in addition to hydrogen sulphide, *vide supra* (105) *b*, γ (small type).

[2] It may also contain silicic acid (in which case it was not entirely pulverulent and soluble in benzene or petroleum spirit).

[3] If organic acids have been detected in the preliminary examination (10, *h*, *i*), the precipitate may also consist of or contain *cinnamic, benzoic,* or *salicylic acid*. Tests for these are made by treatment with ether, or they may be separated as described in (102) and (103), and these anions identified according to Sec. 176 (184).

readily soluble in potassium sulphide solution, and is very sparingly soluble in ammonium sulphide solution, whilst the latter are very slightly soluble in ammonium sulphide solution). The liquid is filtered, and the filtrate treated as in Sec. 170 or 169, and the precipitate as in (40).[1]

(γ) *Hydrogen cyanide is evolved, with or without hydrogen sulphide.* In that case a *cyanide* (and if hydrogen sulphide is simultaneously liberated also a *sulphide*) of an *alkali* or *alkaline earth metal* is present. Under these conditions the precipitate may also contain numerous compounds (such as nickel or silver cyanide, etc.) in addition to those mentioned in (α) or (β). The liquid is boiled in a fume cupboard after the addition of more hydrochloric acid or of nitric acid until all hydrogen cyanide has been expelled, and the resulting solution, or the filtrate from any insoluble residue (which would be examined as in Sec. 179 or Sec. 180), is treated according to Sec. 165. **108.**

II. A hydrochloric acid or aqua regia solution has been obtained.

It is treated according to Sec. 165.

III. A nitric acid solution has been obtained. **109.**

A portion of the solution is diluted with water, and if any turbidity or precipitate (indicating bismuth ion) is formed, nitric acid is added until the liquid becomes clear again, and then hydrochloric acid.

1. *No precipitate is formed.* This proves the absence of silver and mercurous ion. The main solution is treated as in Sec. 165.
2. *A precipitate is formed.* The remainder of the nitric acid solution is treated in the same way as the small portion, the precipitate filtered off and examined as in (103), and the filtrate examined according to Sec. 165.

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[1] Should silicic acid be present in this precipitate, in addition to the sulphides mentioned, it will dissolve, partly at all events, in the *aqua regia* solution, and must be taken into consideration in examining the latter; it may also partly be left in the residue, and must then be treated accordingly (Sec. 182). *Cf.* footnote 2, p. 607.

SEC. 165.[1]

110. Treatment with Hydrogen Sulphide.[2]

Precipitation of cations of Groups V_2. and VI.

A small portion of the clear acid solution is treated with good hydrogen sulphide water until its odour is plainly perceptible on shaking, and the liquid then gently heated, and, after the addition of more hydrogen sulphide water in not too small amount, allowed to stand for some time.

111. 1. *No precipitate is formed*, even after some time. The analysis is continued at Sec. 170 or 169, since lead, bismuth, cadmium, copper, and mercuric ions, and also the ions of gold, platinum, antimony, tin, and arsenic[3] are not present. The absence of ferric ion, chromate ion, and ferricyanogen ion is also indicated.

112. 2. *A precipitate is formed.*

(*a*) *It is pure white, diffused and finely pulverulent*, and does not disappear on the addition of hydrochloric acid. It is separated sulphur and points to the presence of ferric ion.[4] In order to be sure that the sulphur does not contain a small amount of yellow sulphides, the colour of which might be masked by a large quantity of sulphur, about 2 c.c. of benzene or petroleum spirit are added to the liquid, and the tube vigorously and repeatedly shaken.[5] If no coloured suspension appears in the benzene or petroleum spirit layer, the white precipitate consists only of sulphur. None of the substances mentioned in (111) is present. The main solution is treated as in Sec. 170 or 169. If, however, a coloured suspension is seen in the benzene or petroleum spirit layer, the examination is continued as in 113 (*cf.* Chap. III., No. 27).

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[1] *Cf.* the general survey, p. 600, (*b*).

[2] *Cf.* Chap. III., No. 18 (with regard to a nitric acid or *aqua regia* solution also No. 19); also Nos. 21 and 22.

[3] *Cf.* Chap. III., No. 20.

[4] In the presence of sulphite ion, as also of oxidising substances, *e.g.* chromate ion, chlorate ion, free chlorine, and (on continued heating) ferricyanogen ion, sulphur is also precipitated. When chromate ion is present, the colour of the solution changes from reddish-yellow into green, whilst, in the presence of ferricyanogen ion, the solution usually becomes blue, so that the separated sulphur has the appearance of a blue precipitate.

[5] In shaking the test-tube, closed by means of the thumb, it should be noted that, if the thumb is not absolutely clean, metallic sulphides not originally present may be formed at the junction of the aqueous layer and the benzene.

If the separation of sulphur, the original colour of the solution, and the change of colour on the introduction of hydrogen sulphide, have indicated the presence of chromate ion, this is reduced to chromic ion by the addition of an aqueous solution of sulphur dioxide, or, if the latter would produce a precipitate, by heating the liquid with hydrochloric acid after the addition of a little alcohol, or by means of another suitable reducing agent (*cf.* Sec. 101, 5).

(*b*) *It is not pure white.* The examination is continued as in (113). **113.**

A slow current of gaseous hydrogen sulphide is passed through the solution *diluted with water* (and heated to about 70° if there is reason to suppose that arsenate ion is present) until the precipitate separates in a distinctly flocculent form, and a portion of the liquid then filtered, and tested to see whether it remains clear on the addition of a large amount of hydrogen sulphide water (about six to eight times the volume of the liquid). If this is not the case, the main solution is diluted to a further extent with water, and the introduction of hydrogen sulphide continued until the precipitation is complete, after which the liquid is filtered, and this filtrate reserved for testing for cations of Groups I. to IV., Sec. 170 or 169 *et seq.* The precipitate, which will contain the sulphides of the metals of Groups V_2. and VI.,[1] is *thoroughly washed*, without exposing it long to the air (Chap. III., No. 22) (the completeness of washing being ascertained by a test with litmus paper or silver nitrate, *cf.* p. 42), and the examination is continued at (114).

Instead of gaseous hydrogen sulphide, good hydrogen sulphide water may be used for the precipitation. In that case the bulk of the acid or acidified solution is treated, preferably in a small boiling flask, with an excess of hydrogen sulphide water, *i.e.* until the solution, after thorough shaking, has a distinct odour of the gas, and the precipitate does not increase on further addition of the reagent, the contents of the flask then gently heated, the liquid filtered, and the filtrate and precipitate treated as described above.

If the precipitate is yellow,[2] its main constituent will be arsenic, stannic, or cadmium sulphide; if it is orange-coloured, the presence of antimony sulphide is indicated; if brown or black, an ion of at least one of the following metals must be present: lead, bismuth, copper, mercury, gold, platinum, tin. Since, however, a yellow precipitate may also contain small amounts of orange, brown, or even black precipitates without their respective colours being distinctly imparted, the most trustworthy method is always to test every coloured precipitate produced by hydrogen sulphide for all the ions mentioned under 1 (111), the method outlined in the following section being followed.

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[1] Under exceptional conditions the precipitate produced by hydrogen sulphide in an acid solution which has been treated with hydrochloric acid may also contain zinc and iron, *e.g.* zinc when alkali acetates are present, and iron when the solution contains stannic chloride, and only a little free hydrochloric acid (L. Storch, *Zeitsch. anal. Chem.*, **25**, 219) (*cf.* Chap. III., No. 18).

[2] Conclusions drawn from the colour of the precipitate may, under certain conditions, be uncertain (*cf.* Chap. III., No. 21).

SEC. 166.

Treatment of the Hydrogen Sulphide Precipitate with Alkali Sulphide.

Separation of Group V_2. from Group VI.

General Survey.

The precipitate produced by hydrogen sulphide may contain the sulphides of the sixth group and the second division of the fifth analytical group. If members of both groups are present, they are separated by treatment with ammonium (or sodium) sulphide solution, in which the sulphides of the sixth group are soluble, sulpho salts being formed (p. 9), whereas those of the fifth group remain undissolved. The sulphides of the sixth group may be re-precipitated by acidifying the sulpho salt solution.

Since this process, however, is only necessary when members of *both* groups are actually present, a *small portion* of the precipitate should be tested to see whether it dissolves completely in ammonium (or sodium) sulphide solution, or, if this is not the case, the filtered liquid is acidified to see whether anything has dissolved. Only in the latter alternative should the whole of the precipitate be treated in the same way, whilst the remainder of a precipitate which is completely soluble in alkali sulphide solution should be tested directly for members of Group II. as in Sec. 167, and the remainder of a completely insoluble sulphide precipitate should be tested at once for members of Group V_2. as in Sec. 168.

Process in detail.

114. *A small portion of the precipitate produced by hydrogen sulphide in the acidified solution is thoroughly washed* (Chap. III., Nos. 22 and 25) *and treated in a test-tube*[1] with 10 to 20 drops of pale yellow (not dark yellow, see Chap. III., No. 23) *ammonium sulphide solution*, or (if cupric but not mercuric sulphide is present) with *sodium sulphide solution*[2] (see Chap. III., No. 21), *and gently heated for a short time.*

1. *The precipitate is completely soluble in ammonium (or sodium) sulphide solution.* The absence of cations of Group V. (cadmium, lead, bismuth, copper, mercury) is indicated. The remainder of the precipitate (a portion of which was tested with ammonium sulphide solution) is treated as in Sec. 167. **115.**

   If the quantity of hydrogen sulphide precipitate was so small that the whole of it had to be used in the treatment with ammonium sulphide, hydrochloric acid is added to the ammonium sulphide solution, and the resulting precipitate washed and examined as in Sec. 167.

2. *It is insoluble or not completely soluble*, even when heated with more yellow ammonium (or sodium) sulphide. The presence of cations of Group V. is indicated. The liquid is diluted with 4 to 5 parts of water, or with 10 per cent ammonium nitrate solution (if there is reason to suppose that the precipitate produced by hydrogen sulphide contains mercuric or stannic sulphide, Chap. III., No. 26), and then filtered, and the filtrate treated with a slight excess of hydrochloric acid. **116.**

   If the whole of the hydrogen sulphide precipitate had to be treated with ammonium sulphide, only a portion of the solution should be treated with hydrochloric acid.

   (*a*) *Only a pure white turbidity is formed*, which does not yield a coloured deposit on shaking the liquid with benzene or petroleum spirit (*cf.* (112) or Chap. III., No. 27). This turbidity produced by hydrochloric acid is, therefore, pure sulphur. The absence of members of Group VI. (ions of gold, platinum, tin, antimony, and arsenic) is indicated. The remainder of the precipitate obtained in (113) (a portion of which has been digested with ammonium sulphide solution), or the entire precipitate which has been treated with ammonium sulphide and washed, is examined as in Sec. 168.

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[1] If the precipitate is at all bulky, this may easily be done by means of a small spatula of platinum, glass, or horn, whereas if it is scanty the filter should be spread open in a porcelain basin and the whole of it treated with ammonium (or sodium) sulphide solution.

[2] If the solution is blue or green and the filtrate from the hydrogen sulphide precipitate no longer shows this colour, cupric ion is present. If a definite conclusion is not possible, it may almost always be reached by testing the solution with a bright iron rod or with excess of ammonia (Sec. 75, 18, 9). A test for mercuric ion is made by treating a portion of the original solution with stannous chloride. As a rule its presence will already have been indicated by the change in colour of the precipitate produced by hydrogen sulphides (Sec. 74, 6, 3).

117. (*b*) *A coloured precipitate is formed*, or a coloured suspension in the benzene or petroleum spirit layer. This indicates the presence of members of Group VI. in addition to those of Group V. The entire precipitate produced by hydrogen sulphide is treated in the same way as the sample, *i.e.* it is treated with yellow ammonium (or sodium) sulphide solution, and allowed to stand, the supernatant liquid (which must be yellow) is poured on to a filter, the residue in the flask repeatedly treated with yellow ammonium (or sodium) sulphide solution, and the solution filtered each time.[1] The filtrate (or the remainder of the filtrate (116) if the whole of the hydrogen sulphide precipitate had to be treated with ammonium sulphide (114, footnote 1)), which contains the members of Group VI. in the form of sulpho salts, is diluted with water, and, after the addition of hydrochloric acid until the reaction is distinctly alkaline, is gently heated and filtered from the resulting precipitate. This precipitate, containing the sulphides of Group VI. mixed with sulphur, is thoroughly washed, and treated as described in Sec. 167. The residue from the treatment with ammonium or sodium sulphide (containing the sulphides of Group V.) is usually washed with water, except in the presence of mercury, when a 10 per cent. solution of ammonium nitrate is used for the purpose (see Chap. III., No. 25), and is then treated immediately (Chap. III., No. 22) as in Sec. 168.

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[1] If the residue from the treatment with ammonium (or sodium) sulphide does not readily subside, with the result that the liquid cannot be poured off, it should be transferred to the filter, and the latter, after filtration of the liquid, spread open, together with the residue, in a porcelain dish and treated repeatedly as above. If the sulphides are in such a fine state of suspension that the liquid will not yield a clear filtrate, a little solid ammonium nitrate is added, and the whole allowed to stand for some time while gently heated, and then filtered (*cf.* pp. 36 and 44).

SEC. 167.

Detection of the Ions of Group VI.

Ions of Arsenic, Antimony, Tin, Gold, and Platinum.

General Survey.

The sulphides of arsenic, antimony, and tin volatilise when heated in a current of chlorine (or in a current of air containing ammonium chloride and nitrate vapours). Platinum and gold sulphides are decomposed under these conditions. The sulphur which they contain volatilises as chloride, and a residue of the noble metals is left.

Hence the two last may be separated from the three members of Group VI. first mentioned, by sublimation in a current of chlorine (or of air containing chloride and nitrate).

The residue is dissolved in *aqua regia*, the solution evaporated to dryness, the residue dissolved in water, and the gold ion reduced by heating the solution with oxalic acid. The filtrate is evaporated to dryness with ammonium chloride to separate the platinum ion, and the residue treated with alcohol, which leaves the ammonium platinochloride as an insoluble residue.

The sulphides, which are partly dissolved in the aqueous distillate and partly in suspension in the sublimate, are re-precipitated by means of hydrogen sulphide, separated, dried, and ignited with sodium nitrate and carbonate, whereby they are oxidised to stannic oxide, sodium antimonate (which reacts with water to form disodium dihydrogen pyroantimonate), and sodium arsenate. This last is soluble in water, whereas the two first are insoluble, or only sparingly soluble, and are therefore left in the residue when the fused mass is extracted with water.

On heating this residue with hydrochloric acid, and adding a little zinc, preferably in a platinum basin, the metals are reduced and precipitated. They may then be separated by treatment with hydrochloric acid, which dissolves tin but not antimony.

Arsenate ion may be identified in the aqueous extract of the fused mass by acidifying the liquid with nitric acid, and adding ammonium molybdate or magnesia mixture; and stannous ion in the hydrochloric acid solution of the metal by means of mercuric chloride, whilst the antimony, which is left in the insoluble residue, is dissolved by means of nitric and tartaric acids, and precipitated with hydrogen sulphide.

The method of separation may be represented in tabular form as follows :—

There may be present as Sulphides: Au, Pt, Sn, As, Sb The precipitate is mixed with $(NH_4)Cl$ and $(NH_4)NO_3$ and heated in a current of air.

<table>
<tr>
<td colspan="2">Residue Au, Pt as metals It is dissolved in *aqua regia*. The solution when freed from excess of acid and heated with $H_2C_2O_4$ gives—</td>
<td colspan="3">Sublimate. When dissolved in water it contains Sn, Sb, and As as chlorides. Treated with H_2S it gives a—
Precipitate of the three sulphides. This is separated, dried, and fused with $NaNO_3$ and Na_2CO_3. The fused mass treated with water gives—</td>
</tr>
<tr>
<td rowspan="2">Precipitate of Au, recognisable by its colour.</td>
<td rowspan="2">Solution This contains H_2PtCl_6 when evaporated to dryness with NH_4Cl, and the residue treated with alcohol, leaves yellow $(NH_4)_2PtCl_6$</td>
<td colspan="2">Residue. SnO_2 and $Na_2H_2Sb_2O_7$. It is reduced with $HCl+Zn$ to Sn and Sb. These treated with HCl give—</td>
<td rowspan="2">Solution. Na_3AsO_4. Acidified with HNO_3 and heated with $(NH_4)_2MoO_4$ gives a yellow precipitate of ammonium arsenic molybdate.</td>
</tr>
<tr>
<td>Residue. Sb Dissolved in HNO_3+tartaric acid and treated with H_2S gives orange precipitate of Sb_2S_5</td>
<td>Solution $SnCl_2 + HgCl_2$ gives white precipitate of Hg_2Cl_2.</td>
</tr>
</table>

As indicated by the colour of the precipitate or the nature of the substance under examination it may, under certain conditions, be possible to omit the tests for gold and platinum, and to ignite the sulphide precipitate directly. In that case only the portion enclosed in dotted lines need be taken into consideration, or the examination may be restricted to testing for arsenate ion, or to the application of a simple test to prove that the ions of tin and antimony are absent. In this connection the following particulars may be noted :—

118. If the precipitate consisting of the sulphides of Group VI. is pure yellow, the presence of arsenic and stannic ion is probably indicated ; if it is unmistakably orange-yellow, antimony sulphide is undoubtedly present ; whilst if it is brown or black the presence of stannous, platinum, or gold sulphide is indicated.

More than this cannot be inferred with certainty from the colour of the precipitate, and in order, therefore, to be certain under all conditions, it is necessary also to test a yellow precipitate for antimony, gold, and platinum, since small quantities of the sulphides of these metals are completely masked by a large amount of stannic or arsenic sulphide. In many cases, however, it is possible to form an opinion as to the absence of gold and platinum from the general characteristics of the substance under examination, and in the following pages we therefore make a distinction between the case when it may be concluded that gold and platinum are absent, and the case when the facts do not justify such conclusion.

Description of the process in detail. **119.**

1. *There is reason to conclude that gold and platinum are absent.*

(*a*) *The precipitate is yellow.* A small quantity of the thoroughly washed precipitate is heated, not too strongly, on the lid of a porcelain crucible, or on a piece of porcelain or glass.[1]

(α) *No non-volatile residue is left.* Arsenic may be presumed to be present and the other members of Group VI. to be absent. As a confirmatory test a portion of the precipitate is heated with a small quantity of concentrated nitric acid, the liquid diluted and filtered, and the filtrate tested for arsenate ion by heating it with ammonium molybdate (Sec. 90, 9); or a portion is digested with ammonia solution, the liquid filtered, the filtrate evaporated with a granule of sodium carbonate, and the residue fused with potassium cyanide and sodium carbonate in a current of carbon dioxide (Sec. 89, 17). Whether the arsenic was present in trivalent or pentavalent form is determined by the methods given in Sec. 92, 13.

(β) *A non-volatile residue is left.* This indicates the possible presence of antimony, tin, and arsenic sulphides. The analysis is continued at (120).

120. (*b*) *The precipitate is not yellow*, or is not completely volatile (119, β). In that case tin, antimony, or arsenic are possibly present.[2] The remainder of the precipitate is dried

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[1] It is obvious that this preliminary examination may be omitted if the precipitate has a colour other than yellow, and that it is only conclusive when the precipitate submitted to the test has been thoroughly washed.

[2] The method given in (120, *b*) is particularly suitable for the detection of tin, antimony and arsenic when somewhat considerable amounts of both tin and arsenic sulphides are present. If the precipitate contains only very small amounts of these substances, preference should be given to the method described in Sec. 92, 2. This may be represented in tabular form as follows:—

The precipitated sulphides may contain As, Sb, Sn. The moist precipitate is treated with fuming HCl.

Residue: $As_2S_3(As_2S_5)$ Hot concentrated HNO_3 is added. H_3AsO_4 is dissolved. The solution heated with $(NH_4)_2MoO_4$ gives a *yellow* precipitate of ammonium *arsenic* molybdate.	Solution: $SnCl_2$, Sb_2Cl_3. Iron is added.	
	Precipitate. Sb. It is washed, dissolved in HNO_3 + tartaric acid. Solution treated with H_2S gives an orange-red precipitate of Sb_2S_5.	Solution: $SnCl_2$ with $HgCl_2$ gives white precipitate of Hg_2Cl_2.

For further methods of differentiation and separation, see Sec. 92.

completely, separated from the filter,[1] triturated with about 1 part of anhydrous sodium carbonate and 1 part of sodium (*not* potassium) nitrate, and the mixture introduced in small portions into a porcelain crucible, in which 2 parts of sodium nitrate have previously been heated to a state of gentle fusion.

The flame is removed after each addition of a fresh portion, and only replaced beneath the crucible if the substance is not completely oxidised without further heating.

Too strong heating must be *avoided* (Sec. 92, 1, p. 365) After the fusion is complete the mass is poured on to a piece of porcelain or into the lid of a porcelain crucible. When cold, the fused mass (including the portion still adhering to the crucible) is treated with a little cold water, and the insoluble residue (which must be left if antimony or tin is present) is filtered through a moistened filter, and thoroughly washed with a mixture of about equal parts of water and dilute alcohol (Sec. 92, 1, footnote 2). The liquid used for the washing must not be allowed to run into the filtrate. The filtrate and residue are then examined as follows :—

121. (*a*) *Examination of the filtrate for arsenate ion.* The liquid is rendered distinctly acid with nitric acid,[2] heated to expel carbon dioxide and nitrogen trioxide, and a small amount of the solution heated with 2 to 3 c.c. of a nitric acid solution of ammonium molybdate until the liquid is vigorously boiling. If a *yellow* or at all events *yellowish* precipitate is *not* formed (a pure white precipitate would not prove anything), arsenate ion is not present ; if, however, such a precipitate is formed, it indicates the presence of arsenate ion (Sec. 90, 9).

For further confirmation the remaining larger portion of the solution is divided into two parts, one of which is tested with silver nitrate, and the other with magnesia mixture. To the first portion silver nitrate is added in not too small amount, and should any silver chloride be precipitated,[1] the liquid is filtered, and a layer of dilute ammonia solution (1 part of the ordinary reagent with 2 parts of water or, better, 2 parts of alcohol) is poured on to the filtrate down the side of the inclined test-tube, which is then allowed to stand for some time without shaking. The formation of a reddish-brown precipitate, which forms a cloudy suspension at the juncture of the two layers (it may be seen more readily by reflected than by transmitted light), indicates the presence of arsenate ion. If this is present in considerable quantity, the whole of the liquid will be coloured brownish-red by the precipitate of silver arsenate formed, after accurate neutralisation of the free nitric acid, by shaking the contents of the tube with ammonia solution.

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[1] If owing to the small quantity of the precipitate this is not possible, the dried filter paper with the adherent precipitate is cut into small pieces, triturated with sodium carbonate and nitrate and ignited as described above. But since this method has an influence upon the trustworthiness of the test, it should only be used when no more sulphide precipitate can be obtained.

[2] Any precipitate which is produced in this process must be filtered off and, if necessary, examined as in (123). It may contain traces of arsenic which have escaped detection. With regard to its cause, significance, and treatment, see p. 365, footnote 1.

The other portion of the acidified solution is treated **122.** first with ammonia solution and then with a mixture of magnesium sulphate or chloride and ammonium chloride (p. 342, footnote 1), and the sides of the glass vessel gently rubbed with a glass rod. A crystalline precipitate of ammonium magnesium arsenate, which frequently is only formed after the liquid has stood for some time, and is especially deposited on the sides of the vessel, indicates the presence of arsenate ion. As a further confirmation, the precipitate may be washed with ammoniacal water and dissolved in a little dilute hydrochloric acid, the solution gently heated, and the arsenic precipitated by means of hydrogen sulphide, or separated in any way in the elementary condition (*cf.* Sec. 89 and Sec. 90). The methods given in Sec 92, 13 may be used to determine whether the arsenic was originally present in trivalent or in tetravalent condition.

(β) *Examination of the residue for antimony and tin.* Since **123.** any antimony in the residue must be present as white pulverulent disodium dihydrogen pyroantimonate, and any tin as white, flocculent stannic oxide, the appearance of the residue sometimes enables pregnant conclusions as to its nature to be drawn, although, when doing so, it is necessary to bear in mind that occasionally some copper may also be found in this residue, owing to cupric sulphide being slightly soluble in ammonium sulphide or in sodium sulphoarsenate or stannate solutions. This residue is heated with hydrochloric acid in the inverted lid of a platinum crucible or a small platinum basin, the liquid diluted with a little water, and then, regardless whether the substance has dissolved completely in the hydrochloric acid or not, a compact fragment of zinc (free from lead) is added. Stannic oxide, and also pyroantimonate, is reduced by the zinc, and left in the form of the respective metal. *Antimony* may be recognised by the *blackening of the platinum*, either immediately or after some time. As soon as the evolution of hydrogen has nearly stopped, the remainder of the zinc [1] is withdrawn, the zinc chloride solution removed by careful decantation and washing, the metals heated for a short time with hydrochloric acid, and a portion of the solution (which if tin was present must contain stannous chloride) is tested with mercuric chloride (Sec. 87, 10).[1] The separated antimony (and also any copper which may be present) remains almost completely undissolved when heated with hydrochloric acid; it may be dissolved by heating it with nitric acid containing a little tartaric acid, and precipitated for further examination, by means of hydrogen sulphide. If the solution contains copper ion, this may be precipitated as cuprous thiocyanate (Sec. 75, 11) prior to the test with hydrogen sulphide.[2]

---

[1] Silver chloride will be precipitated if the reagents are not quite pure, or if the precipitate has not been thoroughly washed.

The stage of valency in which any tin or antimony detected was originally present may be determined as described in Sec. 92, 11 or 12.

---

[1] Small amounts of tin may have formed adherent deposits on the zinc. They may be detected by dissolving the zinc in hydrochloric acid, and testing the filtered solution with mercuric chloride (Sec. 87, 10).

[2] Should there still be any doubt as to the presence of antimony, since a small quantity of the metal deposited on platinum will dissolve when heated with hydrochloric acid (Sec. 91, 9), the remainder of the hydrochloric acid solution should be tested with tin in a platinum vessel (p. 36).

2. *There is no reason to infer that gold and platinum are not present.* **124.** In that case advantage is taken of the fact that the sulphides of tin, antimony, and arsenic volatilise in the form of chlorides, when heated with an intimate dry mixture of 3 to 5 parts of ammonium chloride and 1 part of ammonium nitrate, whilst auric sulphide and platinum sulphide, when treated in the same way, leave a residue of the elementary metals.

The process is conveniently carried out in the apparatus shown in Fig. 51, the arrangement of which requires no explanation.

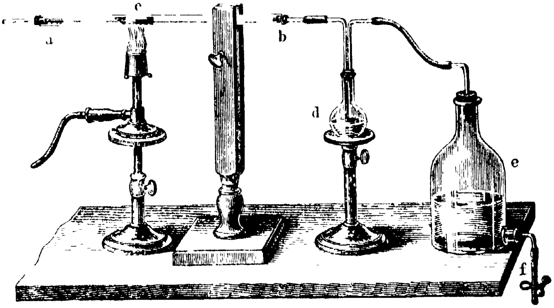

FIG. 51

The tube *ab* is about 30 to 40 cm. long, and about 16 mm. in diameter. The porcelain boat *c* intended to receive the mixture is made in the same way as that shown in Fig. 47 (p. 351), but as a rule a somewhat larger one (7 cm. long) should be used. The boiling flask *d*, which has a capacity of 150 to 180 c.c., is about half filled with water containing a little hydrochloric acid. The flask *e*, which serves as an aspirator, contains about 2 litres.

After the apparatus has been prepared, the *dry* precipitate, consisting of or containing the sulphides of the sixth group, is mixed by careful trituration with about 6 parts of the dry[1] intimate mixture of ammonium chloride and ammonium nitrate, the mixture introduced into the boat, and the latter placed in the tube *ab* in the position shown in the figure. A cork, through which passes a short open glass tube, is inserted into the tube at *a*, the tap *f* (glass tap or screw pinch-cock) opened, and a moderate current of air made to pass from *a* to *b*. The contents of the boat are now heated, gently at first, then gradually more strongly, and finally strongly. A white sublimate is soon formed near *c* (between *b* and *c*), and gradually becomes more pronounced. As soon as the whole of the volatile substances have been expelled from the boat, the tube is allowed to cool, and the boat withdrawn by means of a wire provided with a hook. If the boat contains no residue, gold or platinum is not present, but if a residue of metallic appearance is left, the first part of the test is finished. If, however, the appearance of the residue suggests that the whole of the antimony, tin, or arsenic sulphide has not yet volatilised, it should be covered with a fresh layer of the mixture of ammonium chloride and nitrate, and the boat replaced in the tube and again heated as before. The following tests are applied to the residue and sublimate :—

---

[1] If the precipitate of the sulphides or the ammonium salts is not quite dry, the mass readily froths over the edge of the boat when heated. If any material quantity of water is liberated, the tube may easily break when the condensed water flows over the heated part of the glass. It is, therefore, advisable to fix the tube in the clamp in such a way that *b* is considerably lower than *a*.

(*a*) *Residue.* This is dissolved in *aqua regia*, with the aid of gentle heat (Chap. III., No. 29), and the solution evaporated to a small volume, and tested for gold and platinum ions as in Sec. 86.

(*b*) *Sublimate.* The tube *ab* is washed out with the acidified water (which may sometimes show a white turbidity) previously placed in the boiling flask *d*, the liquid treated with hydrogen sulphide, whether or not any such turbidity is present, and the precipitate separated, washed, and tested for tin, antimony, and arsenic as in (119) to (123).[1]

SEC. 168.

Detection of the Cations of Group V_2.

Lead, Bismuth, Copper, Cadmium, Mercuric Ions.

General Survey.

On boiling the sulphides of the fifth group with dilute nitric acid mercuric sulphide remains undissolved, whilst the other sulphides are converted into nitrates and dissolved. When this solution is treated with sulphuric acid, lead ion is precipitated as sulphate, and may be separated almost quantitatively by evaporating the liquid until practically the whole of the nitric acid has been expelled. The filtrate containing the bismuth, cupric, and cadmium ions gives a white precipitate of bismuth hydroxide when treated with ammonia solution, whilst the cupric and cadmium ions combine with ammonia to form complexes soluble in water. If the ammoniacal solution is evaporated, rendered just acid with hydrochloric acid, and treated with an aqueous solution of sulphur dioxide and with potassium thiocyanate, the cupric ion (owing to its being reduced by the sulphur dioxide to cuprous ion) will be completely precipitated as cuprous thiocyanate. The cadmium may then be precipitated as yellow cadmium sulphide from the filtrate, after removal of the sulphur dioxide.

---

[1] For other methods of separating the ions of gold and platinum from those of tin, antimony, and arsenic, see Sec. 92, 14.

This scheme of separation may be represented in tabular form as follows :—

The portion of the hydrogen sulphide precipitate insoluble in ammonium sulphide may possibly contain : HgS, PbS, Bi_2S_3, CuS, CdS It is boiled with dilute HNO_3

<table>
<tr><td rowspan="4">Black residue : HgS, boiled with $HCl + KClO_3$, gives solution of $HgCl_2$. After boiling off Cl and addition of $SnCl_2$, white precipitate of Hg_2Cl_2, or grey ppt. of Hg</td><td colspan="4">Solution : $Pb(NO_3)_2$, $Bi(NO_2)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2 + H_2SO_4$, evaporated on water-bath until all HNO_3 has been expelled.</td></tr>
<tr><td rowspan="3">Precipitate $PbSO_4$, treated with K_2CrO_4 gives $PbCrO_4$, soluble in $NaOH$ solution treated with acetic acid gives yellow ppt. of $PbCrO_4$</td><td colspan="3">Solution : $Bi_2(SO_4)_3$, $CaSO_4$, $CdSO_4$, $+ NH_4OH$.</td></tr>
<tr><td rowspan="2">Precipitate : $Bi(OH)_3$ Dissolved in a little HCl solution diluted with much water. White turbidity of $BiOCl$.</td><td colspan="2">Solution : $Cu(NH_3)_n(OH)_2$, $Cd(NH_3)_n(OH)_2$; $+HCl$; $CuCl_2$, $CdCl_2 + SO_2 + KCNS$.</td></tr>
<tr><td>Red-white precipitate : $CuCNS$.</td><td>Solution : $CdCl_2$ evaporated to expel SO_2 ; $+H_2S$ yellow CdS.</td></tr>
</table>

Process in detail.

The precipitate which has not been dissolved by ammonium (or sodium) sulphide is thoroughly washed and *boiled with dilute nitric acid* (Chap. III., No. 32). This is best done in a small porcelain basin by heating the precipitate with a little water, and gradually adding nitric acid, while the liquid is continually heated and stirred. A large excess of acid should be avoided (Chap. III., No. 32). **125.**

If the solution turns brown the presence of platinum ion is indicated, this having remained undissolved in the treatment with ammonium sulphide, and then dissolving as nitrate. With regard to the procedure in this case, see Chap. III., No. 31.

126. 1. *The precipitate dissolves, and only light flocculent yellow sulphur separates and remains in the liquid* (Chap. III., No. 32). The absence of mercuric sulphide is indicated. Cadmium, cupric, lead, and bismuth ions may be present. The liquid is filtered from the separated sulphur, and the filtrate freed from the greater part of the nitric acid by evaporation, and treated as follows (or as in Chap. III., No. 37):—

A portion of the liquid is heated with dilute sulphuric acid in not too small a quantity, and allowed to stand for some time.

127. (*a*) *No precipitate is formed.* The absence of lead ion is indicated. The remainder of the liquid is treated with excess of ammonia solution.

128. (*α*) *No precipitate is formed.* Bismuth ion is absent. *If the liquid is blue the presence of copper is proved.* Very minute quantities of cupric ion, however, might be overlooked if merely the colour of the ammoniacal liquid were taken into consideration. In order, therefore, to be certain on this point, and to detect cadmium ion, the ammoniacal liquid is evaporated nearly to dryness, diluted with a little water, and rendered only just acid with hydrochloric acid, and, *if the presence of cupric ion has not already been recognised with certainty by the blue colour* of the ammoniacal solution, a small portion is treated with potassium ferrocyanide. If a reddish-brown precipitate (or in the case of very minute quantities of cupric ion, a brownish-light red turbidity) is produced, *copper* is present.

According to whether cupric ion is present or not, another portion of the liquid is treated as follows:—

129. (*αα*) *Cupric ion is not present.* A portion of the solution is treated with a *little* more hydrochloric acid, and then with hydrogen sulphide water. A *yellow* precipitate indicates *cadmium ion.*

If a pure yellow precipitate is not obtained here, the procedure described in Chap. III., No. 36, is followed. If the precipitate produced in the acid solution by hydrogen sulphide contains zinc sulphide (*cf.* footnote 2, p. 611, the zinc will be found in the hydrochloric acid solution, if necessary, freed from cupric and cadmium ions, as in (129) and (130), and may be precipitated therefrom by the addition of ammonia, or, if necessary, as white zinc sulphide by means of ammonium sulphide.

(*bb*) *Cupric ion is present.* Sulphur dioxide solution **130.** in *good* condition, or hydroxylamine or hydrazine sulphate with potassium thiocyanate is added, and a reddish-white precipitate of cuprous thiocyanate obtained.

If a dark precipitate of cupric thiocyanate is obtained, insufficient reducing agent was present and more must be added.

The precipitate is allowed to subside in a warm place, a portion of the liquid filtered without disturbing the precipitate, and the *clear* filtrate heated to expel sulphur dioxide, and tested for cadmium ion as in (129). (*cf.* Chap. III., No. 36 and Sec. 78, 6).

(β) *A precipitate is formed. Bismuth ion* is present. The **131.** precipitate is filtered off, and the filtrate tested for copper, cadmium (and for zinc ion, which may possibly be present here) as in (128), whilst further tests for bismuth are applied to the washed precipitate. A small quantity of the moist precipitate is transferred to a clock glass by means of a glass rod or a spatula, preferably after taking the filter from the funnel and pressing it with absorbent paper to remove adherent water, and dissolved in the smallest possible quantity of water, and the solution diluted with water in not too small an amount. A milky turbidity confirms the presence of *bismuth.*

If the reaction does not occur when these directions are accurately followed, the precipitate produced by ammonia consisted of other hydroxides, *e.g.* of iron. In that particular case the ammonia precipitate is usually reddish-brown. A test for ferric ion is made by treating the solution with potassium thiocyanate (see Chap. III., No. 35).

(*b*) *A precipitate is produced by sulphuric acid. Lead ion* is **132.** present. The whole of the nitric acid solution is evaporated with sulphuric acid in not too small a quantity in a porcelain basin (Chap. III., No. 34) on the water-bath until the nitric acid has been completely expelled, the residual liquid then diluted with water containing a little more sulphuric acid, and immediately filtered from the insoluble lead sulphate (Sec. 76, 10), and the filtrate tested for bismuth, copper, and cadmium ions (and also for zinc and iron ions, which may possibly be present here) as in (127), whilst the precipitate is washed and invariably examined by one of the methods described in Sec. 78, 3.

133. 2. *The precipitate of the metal sulphides is not completely soluble in boiling nitric acid, but a residue, in addition to the supernatant sulphur, is left.* It is probably (almost certainly if the precipitate is heavy and black, Chap. III., No. 32) *mercuric sulphide.* It is allowed to subside, the solution (which is still to be tested for *lead, bismuth, copper,* and *cadmium ions,* as also for zinc and ferric ion, which may possibly be present here), filtered, and a small portion of the filtrate tested with a large excess of hydrogen sulphide water, and should this produce no precipitate, ammonia and ammonium suphide are added. If no precipitation or coloration results, the absence of other cations of Group V. is proved. If a precipitate or coloration is produced, the remainder of the filtrate is treated as in (126).

The residue, which, in addition to mercuric sulphide, may also contain cadmium sulphide retained by the mercuric sulphide, lead sulphate formed by the action of nitric acid on lead sulphide, also stannic oxide, and possibly also gold and platinum sulphides (since the separation of the sulphides of tin, gold, and platinum from those of the fifth group is frequently incomplete), is washed, and a portion of it tested for mercury[1] by dissolving it in hydrochloric acid containing a little potassium chlorate, and treating the solution with copper or stannous chloride (Sec. 74, 6, 9).

If cadmium and lead have already been detected as in (129) or (132), tin as in (123), and gold and platinum (if they need be taken into consideration) as in (124), a further examination of the residue insoluble in nitric acid is unnecessary (Chap. III., No. 33). Otherwise the following procedure is adopted :—

---

[1] If an aqueous or very dilute hydrochloric acid solution was under examination, the mercury found was present in the original substance as a mercuric compound. If, however, the solution had been obtained by boiling the substance with concentrated hydrochloric acid, or heating it with nitric acid or *aqua regia,* the mercuric ion may have been formed from a mercurous compound originally present.

The remainder of the residue is heated with a concentrated solution of ammonium acetate, and is thoroughly extracted therewith if *lead ion* can be detected with hydrogen sulphide in a portion of the filtrate. The residue, which is usually left, is washed and heated, with access of air, in a porcelain crucible in a fume cupboard, whereby any mercuric sulphide present volatilises. If a residue is left, it is heated with a mixture of equal parts of sodium carbonate and potassium cyanide over a small flame until it just fuses, and the mass then cooled and treated with water. If a metallic powder is left undissolved, it is washed and heated with concentrated hydrochloric acid, the liquid diluted and filtered, and a portion of the filtrate tested for *stannous ion* with mercuric chloride. The remainder of the solution is treated with a moderate excess of sodium or potassium hydroxide, and filtered from any white precipitate remaining undissolved, the latter washed and dissolved in hydrochloric acid, and the solution tested with hydrogen sulphide for *cadmium ion*. Any residue left from the treatment of the metallic powder with hydrochloric acid is heated with *aqua regia*, and the solution tested for *gold* and *platinum* as in Sec. 96. The aqueous solution of the fused mass, however, which contains potassium cyanide, is treated with hydrogen sulphide water, since it may contain cadmium ion.

SEC. 169.

Destruction of Organic Substances in the portion of the material to be tested for Members of Groups I. to IV.

General Survey.

The process outlined in the following sections for the further examination of the substance free from members of Group V. and VI., presupposes that organic substances are not present, since these may have a disturbing influence (Chap. III., No. 39).

Hence, before the substance can be submitted to further examination, it is essential to destroy any organic substances which may be present. (Whether this is necessary will be shown by the preliminary examination (10).) This is done by different methods, using two portions of the substance.

(*α*) By fusing the portion intended for the detection of Groups II. to IV. with alkali carbonate and nitrate, and dissolving the fused mass in dilute hydrochloric acid.

(*β*) By heating the portion intended for the detection of alkali metals with concentrated sulphuric acid.

For this purpose the substance, which is free or has been freed **134.**
from members of Groups V. and VI., and is soluble in water or acid,

is used. That is to say, *either* (*a*) the filtrate obtained in (113); or, if no precipitate was produced by hydrogen sulphide, (*b*) the filtrate from the precipitate produced by hydrochloric acid, as in Sec. 164; or, if hydrochloric acid has produced no precipitate, (*c*) the solution obtained in Sec. 155, after filtration from any residue insoluble in acids (41); *or* (*d*) the original substance itself, if it does not dissolve completely in water or hydrochloric acid, and any solution obtained does not give a precipitate with hydrochloric acid, or with hydrogen sulphide.

Process in detail.

The preliminary examination (10) proved—

(*a*) *The absence of organic substances.* The examination is continued at Sec. 170.

(*b*) *The presence of organic substances.* A portion of the substance is treated as in (135) and another portion as in (136).

135. (*α*) *Portion taken for the detection of members of Groups II. to IV.* According to the conditions in (134) either the greater part of the solution *a*, *b*, or *c* mentioned in (134) is evaporated nearly to dryness and treated with a slight excess of sodium carbonate and a little potassium nitrate, or a portion of the original substance (134, *d*) is mixed with sodium carbonate and potassium nitrate, and in either case the mixture heated in a platinum vessel until the organic matter is destroyed. The fused mass is treated with water, the solution, together with the insoluble particles left in the platinum vessel, is transferred to a glass or porcelain vessel, acidified with hydrochloric acid, and heated (with the addition of a little alcohol,[1] if the solution is yellow, to reduce any chromate ion present to chromic ion (Sec. 101, 5)), until everything has dissolved.[2] The solution is treated as in Sec. 170 (137).

136. (*β*) *Portion taken for the detection of alkali metal ions.* A portion of the solution *a*, *b*, or *c* mentioned in (134) is evaporated in a porcelain basin to dryness, and the residue thus obtained moistened, or, in the case of *d* (134), a portion of the original substance is heated with pure concentrated sulphuric acid in a fume cupboard or in the open air, until the bulk of the sulphuric acid has evaporated, the liquid cooled, diluted, and filtered, and the filtrate treated as in (170).

---

[1] Or any other suitable reducing agent (not sulphur dioxide).

[2] Should a residue insoluble in hydrochloric acid (silicon dioxide) remain, it is examined as in Sec. 179.

SEC. 170.

Precipitation with Ammonia and Ammonium Sulphide.

Separation and estimation of the Members of Group III. (as hydroxides), IV. (as sulphides), and II. (in the form of certain salts). Aluminium, chromic, manganous, zinc, nickel, cobalt, ferrous and ferric ions, also barium, strontium, calcium, and magnesium ion (with phosphate, borate, oxalate, silicate, and fluorine ions).

General Survey.

Since members of the second group can only be separated in the precipitate produced by ammonia and ammonium sulphide when the anions mentioned in the headline are present, it is, as a rule, only necessary to take them into consideration when the original solution was not a neutral aqueous one, but was an acid one.

Small quantities of the alkaline earth metal ions may also be precipitated with aluminium or chromic hydroxide in the absence of the anions mentioned.

If the presence of members of Group II. has to be taken into consideration in the ammonium sulphide precipitate, a somewhat more lengthy process is necessary for their detection (150). It is also advisable to use this process in the case of solutions originally alkaline and such as contain chromic compounds (recognisable by their colour) (Chap. III., No. 17). In other cases the simpler, more easily followed process is sufficient.

A. Simple Process.

(If the original solution was an aqueous one, the absence of material quantities of chromic ion is indicated.)

The precipitate produced by ammonia and ammonium sulphide is treated in the cold with hydrochloric acid *diluted* with hydrogen sulphide water. This leaves the sulphides of cobalt and nickel practically undissolved, although small quantities thereof are dissolved simultaneously with the other metals. The residue is ignited with access of air, dissolved in *aqua regia*, and cobalt ion precipitated from acetic acid solution by means of potassium nitrite (*the conditions described below being rigidly observed*), whilst nickel ion is precipitated by means of sodium hydroxide in the filtrate from the cobalt precipitate.

The hydrochloric acid solution, which has been filtered from the bulk of the nickel and cobalt sulphide, is freed from hydrogen sulphide by boiling, oxidised with nitric acid, and boiled with an excess of sodium hydroxide.

Aluminium and zinc remain in solution in the form of anions. Ferric, manganous, and chromic ions (together with the rest of the cobalt and nickel ions) are precipitated as hydroxides. Zinc ion is detected in the solution by means of hydrogen sulphide, and aluminium ion by means of ammonium chloride or hydrochloric acid and ammonia.

A portion of the precipitate is dissolved in hydrochloric acid, and tested for ferric ion by means of potassium thiocyanate, and another portion is tested for manganese and chromium by fusion with potassium chlorate and sodium carbonate. The former is indicated by a red or green coloration, the latter by a yellow coloration. If manganese is present, the fused mass is dissolved in water, and the solution boiled after the addition of a little *alcohol* or hydrogen peroxide, whereby the manganate ion is reduced and hydrated manganese dioxide precipitated, with the result that the yellow colour of any chromate ion which was formerly masked is rendered visible.

This method of separation may be represented in tabular form as follows :—

<table>
<tr><td colspan="6">Possibly present: CoS, NiS, FeS, MnS, ZnS, $Al(OH)_3$, $Cr(OH)_3$ Treated in the cold with 1 part HCl + 4 parts H_2S water</td></tr>
<tr><td colspan="3">Residue: CoS, NiS, (FeS) ignited, CoO, NiO, (Fe_2O_3) dissolved in *aqua regia*, $CoCl_2$, $NiCl_2$, ($FeCl_3$) Treated with NH_4OH</td><td colspan="3">Solution: $FeCl_2$, $MnCl_2$, $ZnCl_2$, ($NiCl_2$, $CoCl_2$), $AlCl_3$, $CrCl_3$, H_2S boiled off + HNO_3, heated to form $FeCl_3$ + NaOH in excess. Boiled.</td></tr>
<tr><td rowspan="2">Precipitate: **[Fe**$(OH)_3$].</td><td colspan="2">Solution: $Ni(NH_3)_4Cl_2$, $Co(NH_3)_4Cl_2$ Evaporated to dryness. Ammonium salts expelled. Dissolved in *aqua regia*, $CoCl_2$, $NiCl_2$ with Na_2CO_3, precipitate of $CoCO_3$, $NiCO_3$ dissolved in acetic acid + KNO_2.</td><td colspan="2">Precipitate: $Fe(OH)_3$, $Cr(OH)_3$, $Mn(OH)_2$, [$Co(OH)_2$, $Ni(OH)_2$], (*a*) Dissolved in HCl + KCNS: red coloration of **Fe**$(CNS)_3$. (*b*) Fused with $KClO_3$ + Na_2CO_3. Green or red mass K_2**Mn**O_4 or **KMn**O_4. Dissolved in water + alcohol, boiled.</td><td rowspan="2">Solution: $Zn(ONa)_2$, $Al(ONa)_3$, (*a*) + a little H_2S: White ppt. **ZnS**, (*b*) + HCl till acid + NH_3. White precipitate **Al**$(OH)_3$.</td></tr>
<tr><td>Precipitate: yellow K_3[**Co**$(NO_2)_6$].</td><td>Solution: $Ni(C_2H_3O_2)_2$ + NaOH; green precipitate of **Ni**$(OH)_2$.</td><td>Precipitate **Mn**$(OH)_4$.</td><td>**Yellow solution K_2CrO_4.**</td></tr>
</table>

B. *Comprehensive Process.*

If the original solution was acid, certain salts of the alkaline earth metals may also separate with the ammonium sulphide precipitate; if it was alkaline, silicic acid may be present in the precipitate. If a considerable amount of chromic ion is present, the whole of the zinc ion may be precipitated at the same time as the chromic ion, on boiling the solution with sodium hydroxide (p. 260). In such cases a more comprehensive process, including all substances which may possibly be present, should be used; it is based upon the following principles: The ammonium sulphide precipitate is treated with hydrochloric acid diluted with hydrogen sulphide water. The sulphides of cobalt and nickel, together with any silicic acid and calcium fluoride, will be left in the insoluble residue.

A portion of this residue is treated with *aqua regia*, and any insoluble residue tested for silicon dioxide as in the analysis of substances insoluble in acids (Sec. 179), whilst the *aqua regia* solution is tested for nickel and cobalt ion, as in the simple process just described. Another portion is tested for fluorine ion by means of sulphuric acid (etching of glass, or, if silicon dioxide is also present, evolution of silicon fluoride).

The following tests are applied to the hydrochloric acid solution of the ammonium sulphide precipitate:—

(*a*) A portion is tested for barium, strontium, and calcium ions by means of sulphuric acid. Any sulphate precipitate is fused with sodium carbonate, and tested for barium and strontium ions by means of potassium chromate and alcohol.

(*b*) Another portion is freed from sulphuric acid by boiling, oxidised with nitric acid, and examined as follows:—

- (α) One portion is tested for ferric ion by means of potassium thiocyanate.
- (β) A second portion (after neutralisation of most of the acid by means of sodium carbonate) is treated with barium carbonate in the cold, to precipitate ferric, chromic, and aluminium ions on the one hand, and, on the other, anions which, in combination with alkaline earth metal ions, have separated with the precipitates. (In order to effect this precipitation completely in the case of phosphate and silicate ions, ferric chloride is added, and a preliminary test must, therefore, be applied in (α) for ferric ion.) Chap. III., No. 57, c.

The barium carbonate precipitate is boiled with sodium hydroxide solution, whereby aluminium ion is dissolved as aluminate ion, which may be detected in the filtrate by means of hydrochloric acid and ammonia.

The barium carbonate precipitate, which has thus been boiled with sodium hydroxide solution, is fused with potassium chlorate and sodium carbonate. A yellow coloration (chromate ion) indicates *chromium*.

The solution separated from the barium carbonate precipitate is treated with ammonium sulphide, whereby only manganous and zinc ions (together with the rest of the cobalt and nickel ions) can be precipitated as sulphides, whilst alkaline earth metal ions (after removal of the disturbing anions) remain in solution.

This second ammonium sulphide precipitate is dissolved in hydrochloric acid diluted with hydrogen sulphide water (the precipitate of the remainder of the nickel and cobalt sulphides being filtered off), the hydrogen sulphide removed by boiling, and the liquid treated with excess of sodium hydroxide. Manganous ion is precipitated, whilst zinc ion dissolves (as zincate ion) and may be detected in the solution by means of hydrogen sulphide.

The filtrate from the second ammonium sulphide precipitate is freed from barium ion (originally present or introduced into the solution by the precipitation with barium carbonate) and from most of the strontium ion by means of sulphuric acid, and the remainder of the strontium ion and the calcium ion are precipitated from the filtrate by means of ammonium carbonate and oxalate. The filtrate now obtained is tested for magnesium ion by means of sodium ammonium hydrogen phosphate. Further tests may be applied to the ammonium sulphide precipitate for the anions which, in combination with alkaline earth metal ions, are simultaneously precipitated. In this general survey, and in the following table, this last examination is not taken into consideration. For a detailed description of this, reference should be made to (160).

The comprehensive method of separation may be represented in tabular form (pp. 634, 635).

It may be mentioned with reference to both of these methods that it seldom, if ever, happens that *all the substances which might possibly be present* occur in the ammonium sulphide precipitate at the same time. This naturally simplifies the methods to a corresponding extent.

Description of the preceding process in detail. A preliminary test is made to see whether ammonium sulphide produces any precipitate. **137.**

For this purpose there is used—

(*a*) *If organic substances are not present*, the sample which was treated with hydrogen sulphide in (110), or, if hydrogen sulphide produced a precipitate, a portion of the filtrate separated therefrom (113).

(*b*) *If organic substances are present*, a portion of the liquid obtained in the treatment in (135).

In the case of (*a*) a portion of the liquid in which hydrogen sulphide has produced no precipitate, or only a separation of sulphur (110), or the filtrate from the precipitate formed (113), is examined in a test-tube to see whether it is coloured or not (Chap. III., No. 44), and then boiled to expel any hydrogen sulphide still present, treated with a few drops of dilute nitric acid, again boiled, and the colour of the liquid again noted. If a yellow coloration is produced during the boiling with dilute nitric acid, ferric ion is usually indicated, but the coloration may also be due to liberated iodine, which may be recognised by its odour, and should be removed by evaporation (Chap. III., No. 45). If the liquid does not contain sufficient hydrochloric acid to form the requisite amount of ammonium salt (Chap. III., No. 41), a little ammonium chloride is added, and then ammonia solution, care being taken to render the liquid only just alkaline (Chap. III., No. 42). It is then heated, the formation of any precipitate being noted, and finally treated with ammonium sulphide, whether or no a precipitate was produced by ammonia alone.

In the case of (*b*) a portion of the solution obtained in

The Ammonium Sulphide precipitate may possibly cont
$CrPO_4$,—$Ba_3(PO_4)_2$, $Sr_3(PO_4)_2$, $Ca_3(PO_4)_2$, $MgNH_4PO_4$, BaB_2O_4, Sr B
$MgSiO_3$, BaF_2, SrF_2, CaF_2, MgF_2, H

<table>
<tr><td colspan="6">Residue: CoS, NiS, (FeS), H_2SiO_3, CaF_2.</td><td colspan="3">Solution: $FeCl_2$, Mn</td></tr>
<tr><td colspan="5">(*a*) Ignited, treated with HCl + NHO_3, evaporated with HCl to dryness. Residue treated with HCl[1]</td><td rowspan="4">(*b*) Heated with H_2SO_4. HF escapes, recognised by its etching action on glass (**CaF_2**), or if silicic acid is present + SiO_2 + H_2SO_4, heated, **SiF_4** escapes and H_2SiO_3 separates in a drop of water (**CaF_3**).</td><td colspan="3">(*a*) + H_2SO_4.</td></tr>
<tr><td colspan="2">Residue SiO_2, CaF_2 + Na_2CO_3, fused. Mass dissolved in water.</td><td colspan="3">Solution: $CoCl_2$, $NiCl_2$ ($FeCl_3$) + NH_4OH.</td><td colspan="2">Precipitate. $BaSO_4$, $SrSO_4$($CaSO_4$), fused with Na_2CO_3 + H_2O.</td><td rowspan="3">Solut mem of Gr IV an Cas + Mg + 3 p dil alcol Pre tat CaS</td></tr>
<tr><td rowspan="2">Residue: **CaF_2**</td><td rowspan="2">Solution. Na_2SiO_3, (NaF) + HCl evaporated to dryness. Residue treated with HCl. Residue **SiO_2**</td><td rowspan="2">Precipitate **$Fe(OH)_3$**</td><td colspan="2">Filtrate: $Co(NH_3)_4Cl_2$, $Ni(NH_3)_4Cl_2$, evaporated to dryness, ammonium salts expelled. Residue: CoO, NiO dissolved in *aqua regia*, excess of acid removed + Na_2CO_3. Precipitate: $CoCO_3$, $NiCO_3$ + $HC_2H_3O_2$. Solution. $Co(C_2H_3O_2)_2$, $Ni(C_2H_3O_2)_2$ + KNO_2</td><td rowspan="2">Residue: $BaCO_3$, $SrCO_3$ ($CaCO_3$). Dissolved in $HC_2H_3O_2$ + K_2CrO_4
Precipitate: **$BaCrO_4$**.</td><td rowspan="2">Filtrate. Na_2SO_4.
Filtrate: + NH_4OH + dilute alcohol. Precipitate. **$SrCrO_4$**.</td></tr>
<tr><td>Precipitate. yellow **$K_2Co(NO_2)_6$**</td><td>Filtrate $Ni(C_2H_3O_2)_2$ + NaOH, green **$Ni(OH)_2$**.</td></tr>
</table>

(135) is treated, if necessary, with a little ammonium chloride (Chap. III., No. 11), and then carefully with ammonia solution until the reaction is just alkaline (Chap. III., No. 42) and heated, a note being taken whether a precipitate is formed, and is finally treated with ammonium sulphide.

138. (*a*) *A precipitate was not produced either by ammonia or ammonium sulphide.* The analysis is continued at Sec. 171, for iron, nickel, cobalt, zinc, manganese, chromic, and aluminium ions are not present, nor are phosphate, borate, silicate, oxalate, or fluorine ions, together with ions of alkaline earth metals or silicate ion (originally in combination with other cations). (With regard to salts of the alkaline earth metals, however, see Chap. III., No. 46.)

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[1] If all H_2SiO_3 and CaF_2 are simultaneously present in this residue insoluble in HCl, the whole of the H_2SiO_3 or of the fluorine ion or of both may volatilise during the solution in *aqua regia* or in the evaporation with HCl (see Chaps. III., No. 53 and 87).

, NiS, FeS, MnS, ZnS—$Al(OH)_3$, $Cr(OH)_3$, or $AlPO_4$,
$_2O_4$, BaC_2O_4, SrC_2O_4, CaC_2O_4, MgC_2O_4, $BaSiO_3$, $SrSiO_3$, $CaSiO_3$,
part HCl and 4 parts H_2S water.

---

l_2, ($CoCl_2$, $NiCl_2$),—$AlCl_3$, $CrCl_3$—$BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$—H_3PO_4
$H_3B_2O_3$, $H_2C_2O_4$, H_2SiO_3, HF.

(*b*) H_2S boiled off + HNO_3 to convert Fe into Fe···.

<table>
<tr><td>a)</td><td colspan="7">(β) + $FeCl_3$ + Na_2CO_3 until nearly neutral + Ba CO_3</td></tr>
<tr><td>NS,
d
ation
NS)$_3$</td><td colspan="2" rowspan="2">Precipitate: $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$, $Ba_3(PO_4)_3$, BaB_2O_4, BaC_2O_4, $BaSiO_3$, BaF_2 + NaOH, boiled</td><td colspan="5">Solution. $MnCl_2$, $ZnCl_2$, ($CoCl_2$, $NiCl_2$), $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$ + NH_4OH + $(NH_4)_2S$</td></tr>
<tr><td></td><td colspan="2">Precipitate MnS, ZnS (CoS, NiS) + HCl + H_2S</td><td colspan="3">Solution $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$; + H_2SO_4.</td></tr>
<tr><td></td><td rowspan="2">Residue: $Cr(OH)_3$, also $Fe(OH)_3$ and the Ba salts. Fused with Na_2CO_3 and $KClO_3$ Yellow **K_2CrO_4**</td><td rowspan="2">Solution. $Al(ONa)_3$ + HCl, then + NH_4OH Precipitate of **$Al(OH)_3$**</td><td>Residue: CoS, NiS.</td><td>Solution: $MnCl_2$, $ZnCl_2$, ($CoCl_2$), ($NiCl_2$), boiled to remove H_2S, + NaOH</td><td>Precipitate: $BaSO_4$ $SrSO_4$</td><td colspan="2">Filtrate. $SrCl_2$, $CaCl_2$, $MgCl_2$, + $(NH_4)_2CO_3$ + $(NH_4)_2C_2O_4$.</td></tr>
<tr><td></td><td colspan="2">Precipitate $Mn(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$ + Na_2CO_3, fused Green **Na_2MnO_4**</td><td>Solution: $Zn(ONa)_2$ + H_2S, white **ZnS**</td><td>Precipitate. $SrCO_3$ CaC_2O_4</td><td>Solution: **$MgCl_2$**; + $Na(NH_4)HPO_4$, precipitate of **$Mg(NH)_4PO_4$**.</td></tr>
</table>

139. (β) *A precipitate is not produced by ammonia, but is produced by ammonium sulphide.* This indicates the absence of phosphate, borate, silicate, oxalate, and fluorine ions, together with ions of alkaline earth metals (see, however, Chap. III., No. 46), of silicate ion (originally present in combination with other cations, and also of ions of iron, chromium, and aluminium. The analysis is continued at 141).

140. (γ) *A precipitate was produced by ammonia alone.* In this case it is necessary to consider: (*aa*) whether the original solution was aqueous and neutral, and whether its colour indicated freedom from chromic ions; or (*bb*) whether it was acid or alkaline, or whether its colour indicated the possible presence of chromic ion (Chap. III., No. 47). In the former case the analysis is continued at (141), for chromic, phosphate, borate, oxalate, silicate, and fluorine ions, together with the ions of alkaline earth metals, or silicate ion in combination with other cations cannot be present; in the latter case, however, the examination is continued at (150), for all the substances mentioned in (138) have to be taken into consideration.

If the original solution was alkaline, the process outlined in (150) is also followed, but in that case, as a rule, in addition to the cations of the third and fourth groups only silicate ion and aluminium and chromic phosphate need be considered, because it is quite an exception for one of the alkaline earth salts mentioned in (138) to be found in alkaline liquids.

141. 1. *Detection of the cations of the third and fourth groups. If phosphate ion, etc., in association with alkaline earth metal ions, and also chromic ion, are not present*, see Chap. III., No. 46.

The liquid mentioned in (137), a portion of which has been subjected to a preliminary test, is treated with ammonium chloride, and then with ammonia solution, until the reaction is just alkaline (Chap. III., No. 42), and finally with ammonium sulphide, until the liquid when shaken has a distinct odour of the reagent; it is then shaken until the precipitate begins to subside in a flocculent deposit, heated gently for some time, and filtered.

The filtrate, which contains or may contain the members of Groups II. and I., is set aside for subsequent examination as in Sec. 171.

If it is brown or brownish, owing to the nickel sulphide remaining in solution, the nickel ion must be separated (Chap. III., No. 49). The precipitate, however, is washed with water containing a very little ammonium sulphide (Chap. III., No. 49), without allowing it to stand exposed to the air (Chap. III., No. 22), and treated as follows:—

142. It is separated from the filter paper by means of a spatula or fine jet, and treated in the following manner:—

(*a*) *If it is white*, and so cannot contain cobalt or nickel sulphide (or ferrous sulphide), it is heated in a small basin with dilute hydrochloric acid.

(*b*) *If it is black*, it is treated in the cold with a sufficient quantity (Chap. III., No. 51) of a mixture of 1 part of hydrochloric acid of sp. gr. 1·12 (dilute hydrochloric acid) and 4 parts of hydrogen sulphide water (Chap. III., No. 50).

143. (*a*) *It is completely dissolved* (with the exception of separated sulphur). This indicates the absence of nickel and cobalt sulphides, at all events in any considerable quantity.

The solution is boiled until the hydrogen sulphide is *completely* expelled, then treated with nitric acid, again boiled, filtered from any suspended particles of sulphur, and concentrated by evaporation to a *small* residue (*cf.* Sec. 57, 7). This liquid is treated with an excess of potassium or sodium hydroxide solution freshly prepared from solid caustic alkali, and boiled for some time with continual stirring.

(*aa*) *The resulting precipitate is completely soluble in excess of the sodium hydroxide solution.* This indicates the absence of ions of iron, manganese, and chromium (also of traces of nickel and cobalt ions), and the presence of aluminium or zinc ion. A portion of the alkaline solution is tested for zinc ion with a *little* (not an excess) hydrogen sulphide (*cf* Chap. III., No. 52), and the remainder acidified with hydrochloric acid, and heated with a slight excess of ammonia solution. A white flocculent precipitate, which is insoluble even on the addition of more ammonium chloride, indicates *aluminium ion.* **144.**

(*bb*) *The resulting precipitate is insoluble, or does not dissolve completely in excess of sodium hydroxide solution.* The solution is diluted, and the filtrate tested for zinc and aluminium ion as in (144). **145.**

(*aa*) A portion of the *precipitate* is dissolved in hydrochloric acid, and the solution treated with *potassium thiocyanate.* The presence of *ferric ion* is indicated by a blood-red coloration. The original stage of oxidation is determined by testing the original solution with potassium ferrocyanide and potassium thiocyanate (Chap. III., No. 56).

The remainder of the precipitate produced by sodium hydroxide is washed, and a portion of it dried. If it is brown or brownish, and ferric ion is not present, manganous ion is indicated; if the hydrochloric acid solution of the precipitate produced by ammonium sulphide was violet, chromic ion is present.

146. (ββ) To decide whether manganous ion is present (or chromic ion if its presence has not already been recognised by the colour of the solution in the course of the analysis (140)), the dried portion of the precipitate produced by sodium hydroxide is tested by *fusing it with sodium carbonate and potassium chlorate*, and boiling the fused mass with water. If the mass, or its aqueous extract, was green or red, the presence of the ions of *manganese* is indicated. In that case the aqueous solution is treated with a little alcohol, heated, and filtered from the precipitated manganese dioxide (Chap. III., No. 55). If the solution is now yellow, or if the fused mass or its aqueous extract were yellow, the presence of the ions of *chromium* is indicated. If it is not possible to infer with certainty the presence of manganese ions from the green or red colour of the fused mass, a test for manganese compounds is applied to any insoluble residue left by the fused mass, by heating a small portion of it with sodium carbonate in the oxidation flame.

(γγ) If chromic ion is present, and zinc ion has not already been detected in the alkaline solution as in (144), a further portion of the residue is dissolved in hydrochloric acid, and the solution tested for zinc ion (the whole quantity of which may be found at this stage, p. 260, *c*) by evaporating the liquid to a small residue, and (in the absence of ferric ion) adding sodium acetate, and then hydrogen sulphide water in the cold (Sec. 57, 4). If ferric ion is present, the liquid is treated with ammonia in excess, and filtered, and the filtrate acidified, and treated in the cold with hydrogen sulphide water. A white precipitate indicates the presence of *zinc ion* (Chap. III., No. 47).

(δδ) If the ammonium sulphide precipitate contains so little nickel and cobalt sulphide that it dissolves completely when treated with hydrochloric acid (142, *b*), the nickel or cobalt must be present as hydroxides in the precipitate produced as in (143).

If their ions have not been detected in (147) to (149), and traces of them are not to be overlooked, a fresh portion of the hydroxide precipitate is dissolved in hydrochloric acid, and one portion of the solution is tested for cobalt by means of nitroso-β-naphthol (Sec. 60, 18), whilst another portion is treated with ammonia in excess and tested for nickel by means of dimethylglyoxime (Sec. 59, 18). Or another portion of the solution, which has been treated as in ($\gamma\gamma$) and eventually filtered from zinc sulphide, is treated with hydrogen sulphide *while heated.* Any precipitate formed can only contain *nickel* or *cobalt sulphide*, or at all events *zinc ion*, which, owing to the action of chromic ion, has been precipitated by sodium hydroxide (p. 260). It is treated as in (142, *b*, or 143, 147).

(β) *It does not dissolve completely, but leaves a black residue.* **147.** This indicates cobalt and nickel sulphide (*cf.*, however, Chap. III., No. 52). Since, however, especially in the case of precipitates rich in ferrous sulphide, some of this precipitate is often protected against the action of hydrochloric acid by being enveloped in separated sulphur, it is not yet possible to conclude with absolute certainty that cobalt or nickel sulphide is present. The liquid is filtered, the residue washed, and the filtrate tested as in (143), whilst the precipitate, together with the filter paper, is ignited in a porcelain crucible in a current of air until the paper is incinerated.

The residue from the ignition is heated with hydrochloric acid containing a few drops of nitric acid until it has completely dissolved (Chap. III., No. 51). The solution is then diluted with a little water, treated with ammonia solution in moderate excess, and filtered from any precipitated ferric hydroxide. **148.**

A portion of the filtrate, which is blue in the presence of any considerable quantity of nickel compounds, brownish when cobalt compounds are present in any large amount, but shows a less distinctive colour in the presence of both, is then tested with ammonium sulphide. If this produces a black precipitate, the presence of cobalt or nickel compounds is proved.

In that case, the remainder of the ammoniacal filtrate is evaporated to dryness, the ammonium salts completely expelled by gently heating the residue (Chap. III., No. 54), and the following test applied, unless the method described in Chap. III., No. 54, last paragraph, is preferred :—

(*aa*) A portion of the residue is heated in a *borax bead* in the outer and then in the inner flame of a Bunsen burner. If the bead, heated in the oxidation flame, is violet while hot and reddish-brown when cold, and becomes grey and turbid when heated in the reducing flame, *nickel* is present. If, however, it is blue while hot and cold, both in the outer and in the inner flame, *cobalt* is present. Since, however, in the latter case the presence of nickel, and in the presence of much nickel, traces of cobalt frequently cannot be distinctly recognised by means of a borax bead, the following test is made :—

149. (*bb*) The remainder of the residue is dissolved in a little hydrochloric acid containing a few drops of nitric acid, the solution evaporated almost to dryness and rendered alkaline with sodium carbonate. The resulting precipitate is filtered off, dissolved in a little acetic acid, the solution treated with excess of that acid, and finally with *potassium nitrite* (Sec. 60, 15). If a *yellow precipitate* is produced in the liquid acidified with acetic acid (possibly after standing for some time), the presence of *cobalt ion* is confirmed. The liquid is filtered after about 12 hours, and the filtrate tested for *nickel ion* by means of sodium hydroxide (Chap. III., No. 54).

150. 2. *Detection of the cations of the third and fourth groups in the presence of considerable quantities of chromic ion, including cases where there is a possibility that phosphates, borates, silicates, oxalates, or fluorides of alkaline earth metals, or also silicic acid may be* *simultaneously precipitated, i.e.* when the original solution showed a chromium coloration, or an acid (or under certain conditions an alkaline, *cf.* 140) reaction, and yielded a precipitate with ammonia, even in the preliminary examination in (137).

The liquid mentioned in (137) is treated, if necessary, with **151.** a little ammonium chloride, then rendered just alkaline with ammonia (Chap. III., No. 42), and is finally treated with ammonium sulphide until it has a perceptible odour of the reagent when shaken. It is then shaken to promote the separation of the precipitate, heated gently for some time, or allowed to stand loosely covered for some time in a warm place, until the supernatant liquid is clear, and then filtered (Chap. III., No. 48).

The filtrate, which contains or may contain the cations of Groups II. and I., is set aside to be examined later, as in Sec. 171.

If it is brown, the presence of nickel ion is indicated; this must be removed (Chap. III., No. 49). If the filtrate cannot immediately be subjected to further examination, the ammonium sulphide must either be protected from the action of the air, or removed or destroyed (Chap. III., No. 61).

The precipitate, however, is washed with water containing a very little ammonium sulphide (Chap. III., No. 40) and used for the detection of cations by the method described in (152).

Since the original substance has subsequently to be tested for all the anions which it may possibly contain, it is unnecessary at this stage to apply tests for anions present in the ammonium sulphide precipitate; but since it is often advantageous to get to know these at once, especially when any considerable amount of a cation of the alkaline earth metals is present in the ammonium sulphide precipitate, the detection of the anions in question is dealt with after the description of the tests for cations in (160)

The precipitate is separated, immediately after washing, from **152.** the filter by means of a spatula or a fine jet, and examined as in (142). That is to say, it is *either* heated if it is white, and so cannot contain nickel or cobalt sulphide (or ferrous sulphide), with dilute hydrochloric acid; or if it is dark, it is treated in the cold with a moderate excess of a mixture of hydrochloric acid and hydrogen sulphide water (about 1 part of hydrochloric acid of sp. gr. 1·12 and 4 parts of hydrogen sulphide water. Chap. III., Nos. 50 and 51).

(*a*) *A residue is left.* This is filtered off, and the filtrate treated **153.** as in (154). The residue, if black, may contain nickel and cobalt sulphide (*cf.* also Chap. III., No. 52), also silicic acid and sulphur (and possibly also calcium fluoride and oxalate, which are somewhat sparingly soluble in hydrochloric acid).

It is washed, a small portion of the moist precipitate reserved, and the remainder dried, incinerated together with the filter paper, and gently ignited with access of air, so as to burn away the sulphur, and a portion of the residue heated with hydrochloric acid containing a little nitric acid. If *silicon dioxide* is present, it is left as an insoluble residue (p. 634, footnote).

In order to identify this with certainty the residue is fused with sodium carbonate, the fused mass extracted with water, the extract filtered, the filtrate acidified with hydrochloric acid and evaporated to dryness, and the residue treated with hydrochloric acid and water. *Silicon dioxide* must be left as an insoluble white residue (Chap. III., No. 53).

The solution (or the filtrate) is tested for *cobalt and nickel ions* as in (148).

The remainder of the ignited residue is tested for fluorine ion as described in Sec. 111, 6, if silicic acid is absent, or as in Sec. 111, 7, if silicic acid is present. If fluorine ion is detected, the residue left from the treatment with sulphuric acid is tested for *calcium ion* by treating it with a little water, filtering the solution, and adding 1 volume of dilute alcohol (Sec. 36, end of 3).

In order not to overlook any calcium oxalate which may possibly be present in the residue, the smaller portion of the ignited residue reserved above is treated with stronger hydrochloric acid and tested for calcium ion as in (155), and then for oxalic acid (160, *bb*), if calcium is found.

154. (*b*) *No residue is left* (except a little separated sulphur, the purity of which should be ascertained by washing, drying, and ignition). This indicates the absence of nickel and cobalt sulphides, at all events in any considerable proportion. For the detection of smaller quantities, see (146, *δδ*).

The solution is boiled until the hydrogen sulphide has been expelled (Chap. III., No. 57, *c.* 2), filtered if necessary, and tested as follows :—

(*α*) A small portion is nearly neutralised with ammonia, treated with dilute hydrochloric acid, and gently heated for some time. **155.**

(*aa*) *If no precipitate is formed*, from 1 to 2 volumes of dilute alcohol is added. If this produces a white precipitate, the presence of calcium sulphate is indicated. The liquid is filtered, the precipitate treated with water, and the filtrate tested with ammonium oxalate.

Since the precipitated calcium sulphate may also contain traces of strontium sulphate, it is advisable in accurate analyses to test any residue left from the treatment with water for *strontium* by means of the spectroscope (Sec. 35, 10).

(*bb*) *If a precipitate is produced by dilute sulphuric acid*, it may be *barium* or *strontium sulphate*, or possibly calcium sulphate (*cf.* Chap. III., No. 52, especially at the end). It is filtered off and the filtrate treated as in (*aa*). The precipitate is washed, decomposed by fusion with sodium potassium carbonate, the alkaline earth carbonates washed and dissolved in hydrochloric acid, the solution evaporated to dryness, the residue dissolved in water, and the solution tested as in (163).

(*β*) A larger portion is heated with a little nitric acid, and a small sample of the *cold* solution (Chap. III., No. 57, *c*, 2) tested for *ferric ion* by adding potassium ferrocyanide or potassium thiocyanate solution drop by drop. (The original hydrochloric acid solution must be tested with potassium ferrocyanide and potassium thiocyanate to determine whether the iron was present in the form of a ferrous or ferric compound. Chap. III., No. 56.) *The remainder* of the solution is treated with ferric chloride in such quantity that on mixing a drop thereof with a drop of ammonia solution on a clock glass a yellow precipitate is formed (Chap. III., No. 57, *c*, 1), and the liquid then evaporated, preferably on the water bath, to a *small* residue. This is transferred with the aid of a little water to a boiling flask, treated with sodium carbonate, so as *nearly* to neutralise the free acid, and the *still clear* **156.**

cold solution treated with an excess of barium carbonate (Chap. III., No. 57, *c*, 3, 4, and 5), and allowed to stand in the cold until the liquid above the precipitate is clear. The precipitate (*aa*) is filtered off from the solution (*bb*), and thoroughly washed.

(*aa*) The *precipitate* is now boiled for some time with sodium or potassium hydroxide freshly prepared from pure alkali hydroxide (Chap. III., No. 58), the solution filtered, and the filtrate tested for *aluminium ion* by acidifying it with hydrochloric acid, rendering it just alkaline with ammonia, and boiling it.

157. If the solution or the alkali hydroxide contains silicic acid, the precipitate regarded as aluminium hydroxide may also be silicic acid. If there is reason to suppose this to be the case, the precipitate presumed to be aluminium hydroxide is fused with a little potassium hydrogen sulphate on the lid of a platinum crucible, and treated with hydrochloric acid and water. The resulting aluminium sulphate dissolves, whilst silicon dioxide remains undissolved, and the aluminium ion may be precipitated from the solution as hydroxide by means of ammonia.

The portion of the precipitate insoluble in sodium hydroxide solution is tested for *chromium* by fusing it with potassium chlorate, and treating the fused mass with water (Sec. 41, 12). A yellow coloration indicates the formation of *chromate ion*. Should a green or red coloration, due to manganese ion, be produced, the method given in (146) is followed (Chap. III., No. 57, *c*, 5).

(*bb*) The *solution* is treated with a few drops of hydrochloric acid, boiled (to expel all carbon dioxide), and then treated with ammonia and ammonium sulphide.

158. (*aa*) *No precipitate is formed.* The absence of manganous and zinc ions is indicated. The solution, which contains barium chloride, is treated with a slight excess of dilute sulphuric acid, filtered, rendered alkaline with ammonia, and tested with ammonium oxalate.

If a precipitate is formed, the presence of *calcium ion* already detected (155, *aa*) is confirmed. If strontium ion has been found in (155) a little more ammonium carbonate is added, the liquid filtered from any precipitate produced, and the filtrate tested for *magnesium ion* by means of sodium ammonium hydrogen phosphate.

(*ββ*) *A precipitate is formed.* It is allowed to subside, filtered off, and the filtrate treated as in (158). The precipitate, which may consist of the sulphides of manganese or zinc (together with traces of cobalt and nickel), is washed and tested for *manganese, zinc, cobalt,* and *nickel* (if the last mentioned has not already been found in (153) as in (142) to 149)). **159.**

(*γ*) If alkaline earth metal ions have been detected in (*α*) and (*β*), and the anions with which they are in combination in the ammonium sulphide precipitates are to be identified, tests for the anions in question are applied to the hydrochloric acid solution (152) of the precipitate produced by ammonia and ammonium sulphide as in (150), in which examination it is to be noted that phosphate and silicate ions in combination with aluminium or chromic ions may also be present in the precipitate produced by ammonia and ammonium sulphide. **160.**

(*aa*) A portion of the solution is evaporated in a small basin or clock glass on the water bath, and the residue thoroughly dried on the water bath and treated with hydrochloric acid. If silicate ion was present in the solution, an insoluble residue of *silicon dioxide* will be left (p 634, footnote). The solution is then tested for *phosphate ion* by evaporating it with nitric acid, and treating it with ammonium molybdate solution (Sec. 107, 10).

(*bb*) A second portion is concentrated by evaporation, treated with excess of sodium carbonate, boiled for some time, and filtered, and a portion of the filtrate tested for *oxalate ion* by acidifying it and adding calcium sulphate solution. A further portion is slightly acidified with hydrochloric acid and tested for *borate ion* by means of turmeric paper (Secs. 110, 7, and 109, 5).

(*cc*) The remainder of the solution is treated with ammonia, and the precipitate separated, washed and tested for *fluorine ion*, as in Sec. 111, 6 and 7).

SEC. 171.

Separation and Identification of the Cations of Group II. precipitated by Ammonium Carbonate, in the presence of Ammonium Chloride.

Barium, Strontium, and Calcium Ions.

General Survey.

The solution, which still contains members of Groups I. and II., is treated with ammonium carbonate to precipitate barium, strontium, and calcium ions as carbonates, the precipitate dissolved in acetic acid, and barium ion precipitated as barium chromate by means of potassium chromate. The filtrate is treated with ammonium carbonate to re-precipitate strontium and calcium ions, the precipitate dissolved in hydrochloric acid, the solution neutralised with ammonia, and calcium ion precipitated as calcium potassium ferrocyanide from the hot solution by means of potassium ferrocyanide. Strontium ion is precipitated from the filtrate by means of ammonium carbonate.

The separation of the three alkaline earth metals may be represented in tabular form as follows :—

<table>
<tr><td colspan="3">There may be present in the precipitate produced by ammonium carbonate: $BaCO_3$, $SrCO_3$, $CaCO_3$; the precipitate is dissolved in acetic acid, $+K_2CrO_4$</td></tr>
<tr><td rowspan="2">Precipitate: $\mathbf{BaCrO_4}$.</td><td colspan="2">Filtrate: $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$, $+(NH_4)_2CO_3$. Precipitate of $SrCO_3$, $CaCO_3$. Dissolved in HCl, CO_2 boiled off, solution rendered just alkaline with NH_4OH; $+K_4Fe(CN)_6$, boiled</td></tr>
<tr><td>Precipitate: $\mathbf{CaK(NH_4)Fe(CN)_6}$.</td><td>Filtrate: $+(NH_4)_2CO_3$, white precipitate of $\mathbf{SrCO_3}$.</td></tr>
</table>

Process in detail.

161. *A portion of the solution,* which can now contain only members of Groups I. and II., *is tested with ammonium carbonate to determine whether barium, strontium, or calcium ions are present.*

For this purpose a small quantity of the solution (141) *or* (151), *filtered from the ammonium sulphide precipitate* (and if necessary treated as in Chap. III., No. 61), *is treated with ammonium carbonate and gently heated* (not to boiling point) *for some time; or, if ammonium sulphide has produced no precipitate, a fresh portion of the clear solution used in* (137) *is taken, after being treated, if necessary, with ammonium chloride and rendered alkaline with ammonia.*

Since the presence of a large quantity of ammonium salts has some influence on the precipitation of barium and calcium carbonates, it is better in the case of very accurate analyses, when a precipitate has been produced by ammonium sulphide, or if the original solution contains a large amount of ammonium salts, not to use the filtrate immediately, but first to remove the ammonium salts from the whole of it. For this purpose it is evaporated at once to dryness, or is treated with lead peroxide, or acidified with hydrochloric acid, the solution boiled until the separated sulphur has agglomerated, and filtered, and the filtrate evaporated to dryness (Chap. III., No. 61).

In either case the ammonium salts are completely eliminated by gentle ignition, the residue moistened with hydrochloric acid, diluted with water, filtered if necessary, treated with a little more ammonium chloride if required, and tested with ammonium carbonate as described above (Chap. III., No. 62).

If the filtrate from the ammonium sulphide precipitate was brownish or brownish-black, owing to the presence of dissolved nickel sulphide, the latter must be completely removed by means of acetic acid as in (161) prior to making the test (Chap. III., No. 49).

1. *No precipitate is formed.* This indicates the absence of any considerable amount of barium, strontium, or calcium ions. In order to detect even traces of these, a little ammonium sulphate (prepared by treating dilute sulphuric acid with excess of ammonia) is added to a second portion of the solution. If a turbidity is produced, the presence of traces of barium ion is indicated. A third portion is treated with ammonia and ammonium oxalate, and if a turbidity is produced, possibly only after standing for some hours, traces of calcium are present. The remainder of the solution is then treated as in Sec. 172, after removal of any traces of barium or calcium ion by means of the reagents used for their detection.
2. *A precipitate is formed.* The presence of *calcium, barium,* or *strontium* ion is indicated. The whole of the liquid, a portion of which was tested with ammonia and ammonium sulphide, is treated in the same way as the sample, gently heated and filtered from the resulting precipitate, and a portion of the filtrate tested for any traces of barium or calcium ion which may **162.**

possibly be present, by means of ammonium sulphate and ammonium oxalate (161). If found, these ions are separated by means of the same reagents, and the liquid, now completely freed from barium, strontium, and calcium ion, is tested for magnesium ion as in Sec. 172. The precipitate produced by ammonium carbonate is washed with water containing a little ammonia. It is then dissolved in acetic acid, the solution evaporated on the water bath until most of the acetic acid has been expelled, and the residue treated with water, and filtered if necessary.

163. A larger portion of the solution is heated to boiling point, if necessary, after the addition of three or four drops of acetic acid, then treated with sufficient potassium chromate solution to make the liquid yellow, and again boiled. If any odour of acetic acid should still be perceptible, a little more potassium chromate solution is added, and the mixture allowed to stand for an hour.

(*a*) *No precipitate is formed.* Barium ion is absent. The rest of the solution is treated in the same way as the hydrochloric acid obtained in (165).

164. (*b*) *A precipitate is formed. Barium ion* is present. The precipitate is filtered off, and the filtrate allowed to stand for some time in a warm place.

(*α*) *No precipitate is formed.* Strontium and calcium ions are absent.

165. (*β*) *A precipitate is formed.* It is filtered off, washed, and dissolved in the smallest possible quantity of dilute hydrochloric acid.

A large portion of this solution (and in the case of (163, *a*) a second large portion of the solution from the end of (163)) is rendered just alkaline with ammonia solution free from carbonate, heated to boiling point, treated with excess of potassium ferrocyanide solution, and again heated.

(*aa*) *No precipitate is formed.* Calcium ion is absent; *strontium* ion is present. As a confirmatory test, the solution, a portion of which has been tested with potassium ferrocyanide, is treated with calcium sulphate solution, which ought to produce a precipitate after some time; confirmation is also obtained by means of the spectroscope.

(*bb*) *A precipitate is formed. Calcium ion* is present. **166.** The liquid is filtered, the filtrate, after a test has shown that no further precipitate is produced by potassium ferrocyanide, is treated with ammonium carbonate and allowed to stand for some time.

(*αα*) *No precipitate is formed.* Strontium ion is absent.

(*ββ*) *A precipitate is formed. Strontium ion* is present.

As a confirmatory test, the precipitate is filtered off and tested spectroscopically; or it is dissolved in hydrochloric acid, the solution evaporated to dryness on the water bath, the residue taken up with water, and the solution treated with calcium sulphate solution. A precipitate appearing *after some time* proves the presence of *strontium ion.*

SEC. 172.

Detection of Magnesium Ion.

General Survey.

The *detection* of the presence of magnesium ion is effected by means of the characteristic precipitate of crystalline magnesium ammonium phosphate. The filtrate from this precipitate, however, is unsuitable for the detection of alkali metal ions. Hence, only a portion of the solution which has been freed from the members of Groups III. to VI., and from barium, strontium, and calcium ion, is tested for magnesium ion. Should, however, magnesium ion be found, it is *separated,* prior to applying the tests of alkali metal ions, *by another method,* described in Sec. 173.

Process in detail.

A portion of the liquid in which ammonium carbonate or sulphate or oxalate has produced no precipitate (161), *or of the filtrate from the precipitate produced in* (162), *is treated with ammonium chloride* (*if an ammonium salt is not already present*) *and then with about a third of its volume of ammonia solution, followed by sodium ammonium hydrogen phosphate, and if a precipitate does not appear immediately, the sides of the glass vessel are gently rubbed with a glass rod, and the whole allowed to stand for some time.* **167.**

1. *No precipitate is formed.* Magnesium ion is absent. The analysis is continued at Sec. 173 (168).
2. *A crystalline precipitate is formed. Magnesium ion* is present. *Tests for alkali metal ions* are applied as described in Sec. 173 (169, *b* or *c*).

Magnesium ammonium phosphate is *always crystalline*, as may readily be recognised by separating the liquid, after standing for some time, from the sides of the vessel on which the separated precipitate has deposited (by inverting the test-tube closed with the thumb, or inclining the flask). If, however, only a slight flocculent precipitate is produced by sodium ammonium hydrogen phosphate, the fact does not justify the conclusion that magnesium ion is present. Such a precipitate may be aluminium phosphate (or possibly barium or calcium phosphate) (Chap. III., No. 62). It is filtered off, and treated with a little acetic acid (in which aluminium phosphate is insoluble), the solution filtered, and the filtrate (which must not give a turbidity with ammonium sulphate and oxalate, or if so must be filtered) is treated with ammonia and a few drops of sodium ammonium hydrogen phosphate solution. If magnesium ion was present, a *crystalline* precipitate is *now* obtained (*cf.* also Chap. III., No. 64).

SEC. 173.

Detection of Potassium and Sodium Ions.

General Survey.

The examination to determine whether any alkali metal ion is present consists in evaporating the solution, which is free from other cations, to dryness, volatilising any ammonium salts which may be present, and noting whether a non-volatile residue is left after gentle ignition. The aqueous solution of this residue is tested with platino-hydrochloric acid or sodium hydrogen tartrate for the presence of potassium ion, and with disodium dihydrogen pyroantimonate for sodium ion.

An essential condition for these tests is the preliminary removal of all disturbing substances. In by far the greater number of cases the solution mentioned in (167, 1) is already free from cations of Groups II. to VI. The residue from its evaporation and ignition need, therefore, only be tested with barium chloride to ascertain that no disturbing anions are present (Chap. III., No. 66). If no precipitate is produced, the solution may be directly evaporated and the residue gently ignited. If, however, barium chloride produces a precipitate, such precipitate must be filtered off and the excess of barium ion separated from the filtrate. If a precipitate was obtained in (167, 2), magnesium ion must also be separated prior to the evaporation, and if organic acids were present, so that the substance which had been treated with sulphuric acid, as described in (136), has to be used, it is also necessary to separate from it the sulphuric acid, any cations of Groups II. to IV. still present, together with any anions which might interfere with the examination. In either of these cases the solution is also treated with barium chloride until the whole of precipitable anions have been removed, and then with barium or calcium hydroxide to precipitate the cations of Groups III. and IV., and also magnesium ion as hydroxides.

In the three last-mentioned cases a filtrate is thus obtained, which, in addition to any alkali metal ions that may be present, may also contain barium ion and possibly strontium and calcium ions. These three ions are precipitated by means of ammonium carbonate (and, if necessary, also by means of ammonium oxalate), and a solution is now obtained, which, on evaporation, leaves a residue, which is then ignited.

Process in detail.

(*a*) *If the original substance contains no organic substances, and magnesium ion has not been detected in* (167), a portion (not too small) of the solution mentioned in (167) is evaporated to dryness, preferably in a platinum basin or on a platinum crucible cover, and the ammonium salts expelled by gentle ignition. **168.**

(*α*) *No residue is left.* Potassium and sodium ions are absent (Chap. III., No. 67). The analysis is continued at (172). **169.**

(*β*) *A residue is left.* It is dissolved in a little water; or, if it is insufficient in quantity, the residue obtained in the same way, by evaporating a larger quantity of the solution in a porcelain basin and igniting the residue, is used, and a portion of the solution is treated with barium chloride.

(*aa*) *No precipitate is formed.* Anions which might interfere are not present. Potassium or sodium ion is present.

A further portion of the solution is tested with ammonia and ammonium carbonate, to prove that no residual traces of barium, strontium, or calcium ions or of silicon dioxide are present in the residue (Chap. III., No. 69). If a precipitate is produced by these reagents, the whole of the remainder of the solution of the ignited residue is treated with the same reagents, allowed to stand for some time and filtered, the filtrate evaporated to dryness, and the residue ignited to expel ammonium salts, and dissolved in a little water. This solution, or the solution of the first ignition-residue, if it has remained clear on the addition of ammonia and ammonium carbonate, is treated as follows:—

The examination is continued as in (171), *i.e.* portions of the solution of the residue are tested as there described in (α), (β), and (γ).

(*bb*) *A precipitate is produced by barium chloride.* Anions which will interfere with the test are present. The analysis is continued as in (170).

(*b*) *If the original substance was free from organic substances, but magnesium ion was found in* (167), the whole of the solution under examination is evaporated to dryness in a porcelain crucible, the residue gently ignited to expel ammonium salts (Chap. III., No. 68), and then heated with water, and the analysis continued as in (170).

(*c*) If the original solution contained organic substances, so that a solution of the portion which has been treated with sulphuric acid in (136) is to be examined, the procedure described in (170) is followed.

170. The solution to be tested for alkali metals, of the residue obtained by ignition in (169, β, *bb*) or (169, *b*), or the solution mentioned in (169, *c*), is treated with barium chloride, and if a precipitate is produced, more of the reagent is added, until everything precipitable has been precipitated; and then, if the solution mentioned in (169, *b* or *c*) is present (*i.e.* if magnesium ion or other cations are to be separated), barium hydroxide solution or a thin milk of lime is added until the reaction is distinctly alkaline (until the colour of turmeric paper becomes a pronounced brown), the liquid boiled for some time and filtered, and the precipitate thoroughly washed (Chap. III., No. 69).

The filtrate and washings are treated with ammonia, ammonium carbonate, and ammonium oxalate in slight excess, gently heated for some time and filtered, and the precipitate thoroughly washed. The solution is evaporated to dryness, the ammonium salts expelled, and the residue dissolved in water. The solution is tested with a few drops of ammonium carbonate and oxalate solutions to see whether any precipitate is still formed, filtered from it if necessary, the filtrate evaporated to dryness, the small amount of ammonium salts expelled, and a note taken as in (168) whether a residue is left.

(*a*) *No residue is left.* Potassium and sodium ions are absent (Chap. III., No. 67). The analysis is continued at (172).

(*b*) *A residue is left. Potassium or sodium ion* is present. It is **171.** dissolved in a *little* water, and the solution (which must remain clear when treated with *ammonium carbonate*, Chap. III., end of 69) is divided into three parts and tested as follows :—

(*α*) With platino-hydrochloric acid (Sec. 28, 3).

(*β*) With sodium hydrogen tartrate (Sec. 28, 4).

If a yellow crystalline precipitate is formed in (*α*), and a white crystalline precipitate in (*β*), *potassium ion* is present (Chap. III., No. 70).

(*γ*) After it has been proved that the solution has not an acid reaction, and if so has been neutralised with a little potassium carbonate solution, dipotassium dihydrogen pyroantimonate (Sec. 29, 3) is added.

If a white *sand-like* precipitate is formed, *sodium ion* is present (In applying this test all the precautions given in Sec. 29, 3, must be observed.)

The detection of ammonium ion is effected as in (172).

SEC. 174.

Detection of Ammonium Ion.

The original substance must be used for the *detection of ammonium ion*, since ammonium salts are frequently used for the **172.** detection or separation of cations. A little of the substance, or a small portion of the solution, is triturated with an excess of solid calcium hydroxide, with the addition of a little water if necessary. If a gas with an odour of ammonia is liberated, and this turns moistened red litmus paper blue, and produces white fumes on contact with a glass rod which has been dipped in acetic acid, *ammonium ion* is present. The test is most sensitive when the mixture is stirred in a small beaker, the mouth of which is then covered with a clock glass, upon the under-side of which is placed a strip of moistened turmeric or red litmus paper. Care must be taken that there are no particles of calcium hydroxide upon the edge of the beaker which might act upon the test paper.

MIXED COMPOUNDS.

A. Substances soluble in water.

Detection of Anions.

SEC. 175.

I. In the absence of Organic Anions.

General Survey.

For the detection of anions which have not already been found in the examination for cations, portions of the neutralised solution are tested with the group reagents barium chloride and silver nitrate, with subsequent acidification, for members of the first group (and especially for sulphate ion if a positive result is obtained) and for members of the second group respectively, and separate portions of the original substance are then tested for the individual members of the third group. Individual reactions are used for the detection of the different anions of the third group, in so far as their presence has not been proved by means of the group reagents. If members of the second group are detected by means of silver nitrate, test reactions for individual substances are also applied in this case, and if several of them are present together a *process of separation* must be used (see Chap. III., No. 73).

Process in detail.

In the first place it is necessary to consider which anions can combine with the cations detected, to form compounds soluble in water, and to bear these in mind in the following scheme of examination. In this connection Table I. given in Appendix IV. will be found useful by beginners. Since the process described in the following pages is most simple and trustworthy when no other cations than those of the alkali metals are present, it appears to be the most suitable course to precipitate any other cations which may be present, by heating the solution with sodium carbonate, prior to the examination for anions, and then to apply the tests to the filtrate.

1. *Arsenite and arsenate ions*, and also *carbonate sulphide*, *chromate*, *ferricyanogen*, and *silicate ions*, will, as a rule, have been recognised already in the preliminary examination or in the course of the tests for cations (see Secs. 150, 164, 165, and 167). Chromate ion may also be readily recognised by the yellow or reddish-yellow colour of the solution. In doubtful cases a test is made with lead acetate after the addition of acetic acid (Sec. 101, 8). **173.**

2. The reaction of the solution is determined, and, if it is neutral, a larger portion is rendered *exactly* neutral with nitric acid or with ammonia. Should a precipitate be formed (possibly of silicic acid, magnesium hydroxide, etc.) it must be filtered off. If a gas is evolved during the neutralisation, it should be tested as in (105) for carbonate, sulphide, and cyanide ions, and the gas expelled by boiling (in any case in a fume cupboard, in case it is not merely carbon dioxide). Of this liquid four portions are taken for the tests in 3, 4, 7, and 8. **174.**

3. A portion of the clear neutral solution obtained in 2 is tested with barium chloride or, if the solution contains lead, silver, or mercuric ion, with barium nitrate. **175.**

   (*a*) *No precipitate is formed.* The analysis is continued at (176), since sulphate, phosphate, oxalate, silicate, chromate, arsenite, and arsenate ions, or any considerable amount of borate or fluorine ions are absent.

   If any considerable quantity of ammonium salts is present in the solution, this test is not so conclusive, because ammonium salts have a more or less pronounced solvent influence on the barium salts of most of the acids mentioned (but not on barium sulphate). The precipitation of barium borate is also considerably affected, or even prevented, by the presence of alkali salts (see Chap. III., No. 72).

   (*b*) *A precipitate is formed.* The liquid is diluted and hydrochloric or nitric acid added; if the precipitate is insoluble or only partially soluble, *sulphate ion* is present (*cf.*, however, Chap. III., No. 76). **176.**

4. Silver nitrate is added to a further portion of the neutral clear solution (see 2).

   (*a*) *No precipitate is formed.* The analysis is continued at (181), for neither chlorine, bromine, iodine, cyanogen,[1] thiocyanogen, ferrocyanogen, ferricyanogen, or sulphide ions are present, nor phosphate, arsenate, arsenite, chromate, oxalate, or silicate ions, nor, if the solution was not too dilute, any borate ion.

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[1] The fact that the cyanogen in mercuric cyanide is not detected by silver nitrate was mentioned in (73).

177. (*b*) *A precipitate is formed.* The colour is noted, and the liquid then *shaken with nitric acid.*

Silver chloride, bromide, cyanide, thiocyanate, ferrocyanide, oxalate, silicate and borate are white;[1] silver iodide, orthophosphate, and arsenite are yellow; silver arsenate and ferricyanide brownish-red; silver chromate purple-red; and silver sulphide black.

178. (*a*) *The precipitate dissolves completely.* The analysis is continued at (181), for neither chlorine, bromine, iodine, cyanogen, thiocyanogen, ferrocyanogen, or ferricyanogen ion is present, nor is sulphide ion.

(*β*) *A residue is left.*[2] This indicates the presence of chlorine, bromine, iodine, cyanogen, thiocyanogen, ferrocyanogen, or ferricyanogen ions, and if it is black or blackish, also of sulphide ion. If necessary, the presence of sulphide ion may be readily proved by mixing a further portion of the original solution with an alkaline lead solution (prepared by treating a solution of lead acetate or nitrate with sodium hydroxide solution until the resulting precipitate has re-dissolved).

(*aa*) A fresh portion of the original solution, or of the liquid which has been treated with sodium carbonate and filtered, is treated with a large drop of carbon bisulphide and a small quantity of a solution of nitrous acid in sulphuric acid (potassium nitrite and sulphuric acid), and the tube shaken. If the carbon bisulphide becomes violet in colour, *iodine ion* is present. A little fresh chlorine water is carefully added, whether or no there was a violet coloration, and the tube again shaken. If the carbon bisulphide was coloured violet through the separation of free iodine, the addition of chlorine water is continued until the violet colour just disappears, and a small additional quantity then added. If the carbon bisulphide becomes reddish-yellow, either immediately or after the violet coloration has disappeared, *bromine ion* is present (*cf.*, however, *cc*; also Chap. III., No. 73).

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[1] If organic anions are present, a precipitate formed in a very concentrated solution may also be silver acetate.

[2] Under certain conditions precipitates of cinnamic, benzoic, or salicylic acids (soluble in ether) may appear.

(*bb*) A small portion of the liquid mentioned in (*aa*) is treated with a little hydrochloric acid and tested with two or three drops (*not more*, *cf.* Chap. III., No. 74) of ferric chloride solution. A red coloration indicates *thiocyanogen ion*, and a blue precipitate *ferrocyanogen ion*. If the latter is obtained, a further portion of the liquid mentioned in (*aa*) is acidified with hydrochloric acid and shaken with ether, and the ethereal layer separated and tested for *thiocyanogen ion* with ferric chloride. Another portion of the liquid is tested for *ferricyanogen ion* (*i.e.* if the colour of the silver nitrate precipitate indicated that it might be present) by means of a freshly-prepared solution of ferrous sulphate, obtained by heating pure iron wire with dilute sulphuric acid. **179.**

(*cc*) *Cyanogen ion*, if present in an alkali cyanide soluble in water, may usually be recognised at once by the odour of hydrocyanic acid emitted by the substance, this being more pronounced on the addition of a little dilute sulphuric acid. If ferrocyanogen or ferricyanogen ion is not present, the cyanogen may be detected in the liquid mentioned in (*aa*) by means of ferrous sulphate, ferric chloride, and sodium hydroxide, with the subsequent addition of hydrochloric acid as in Sec. 120, 7. For its detection in the presence of those ions, see Sec. 125, 4.

Since cyanogen ion materially interferes with the detection of iodine and bromine ions by means of nitrous acid (or chlorine water) and carbon bisulphide, a negative result of the test in (*aa*) is not a conclusive proof of the absence of iodine or bromine ion if cyanogen ion is present. In order to detect these ions in this case, it is best to destroy the cyanogen ion beforehand, and to proceed as described in Sec. 125, 5.

180. (*dd*) If iodine, bromine, cyanogen, thiocyanogen, ferrocyanogen, ferricyanogen, and sulphide ions are not present the precipitate insoluble in nitric acid was silver chloride, and the presence of *chlorine ion* is proved.

If, on the other hand, one or more of these other substances was present, a special examination for chlorine ion is necessary, especially if it is not possible to conclude with certainty from the relative proportions of the precipitates that chlorine ion is present.[1] In such exceptional cases one of the methods given in Sec. 125, 8, is used.

181. 5. *Chlorate ion* may be recognised by the yellow coloration which is obtained on introducing a little of the original substance, or of the solid residue left on evaporation, into concentrated sulphuric acid in a clock-glass (Sec. 131, 7).

6. *Nitrate ion* is detected by testing a portion of the original solution with ferrous sulphate and sulphuric acid (Sec. 130, 6).

The presence of some other anions may interfere with or prevent this reaction. If such anions (especially chlorate, chromate, iodine, or bromine ion) were present, they must be either destroyed or removed. In the case of chlorate ion this is effected by ignition with sodium carbonate (Sec. 132, 3); chromate ion is reduced with sulphur dioxide, and the chromic ion precipitated by ammonia; whilst iodine and bromine ions are precipitated by means of silver sulphate. Nitrate ion may also be detected as in Sec. 130, 16.

Tests for *phosphate*, *oxalate*, *silicate*, *borate*, and *fluorine ions* still remain to be applied. In the case of the three first ions, they need only be made when both barium chloride and silver nitrate have produced a precipitate (175, *b*), (176), Chap. III, No. 72.

182. 7. In testing for *phosphate ion* a portion of the neutral solution (174) is treated with a clear mixture of magnesium chloride, ammonium chloride, and ammonia solutions (Sec. 107, 7). Very small quantities of phosphate ion are detected most readily by means of ammonium molybdate (Sec. 107, 10). If arsenate ion is present, it must be separated beforehand, whatever method of examination is used, by means of precipitation with gaseous hydrogen sulphide, from the solution previously acidified and heated to about 70°.

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[1] If, for example, silver nitrate produced an abundant precipitate which was insoluble in nitric acid, whilst in the further examination only traces of iodine or bromine ion were found and other anions of the second group were absent, no further proof is required of the presence of chlorine ion.

8. For the detection of *oxalate ion* and *fluorine ion*, calcium chloride is added to a fresh portion of the neutral solution prepared as in (174), and if a precipitate is formed acetic acid is added. If no precipitate is obtained (or only a precipitate which dissolves readily in acetic acid), oxalate and fluorine ions are not present; if, however, the reverse is the case, although it is not yet possible to form a definite conclusion as to the presence of these anions (Chap. III., No. 75), there is reason for testing the precipitate for them. In that case, portions of the original substance are tested for *oxalate ion* [1] as in Sec. 110, 10, and for *fluorine ion* as in Sec. 111, 6. Since, however, many oxalates cannot be precipitated from their solutions by means of calcium chloride (see p. 432, 4), a direct test for oxalate ion [1] should always be made as in Sec. 110, 10, when heavy metals are present.

9. For the detection of *borate ion*, a portion of the original solution, or of the filtrate from the sodium carbonate precipitate, is slightly acidified with hydrochloric acid, and tested with turmeric paper (Sec. 109, 5). **183.**

Since chlorates, chromates, and iodides interfere with, or prevent the reaction, it is necessary to destroy or remove these ions, if present, prior to applying the test for borate ion (*cf.* 181. 6). Any nitrites present, which also have a disturbing influence upon the test, may be destroyed by treating the acidified liquid with bromine, the excess of which is subsequently removed by boiling.

10. Should *silicate ion* not yet have been found in the examination for cations, a portion of the solution is acidified with hydrochloric acid and evaporated to dryness, and the residue treated with hydrochloric acid (Sec. 115, 3).

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[1] If the substance contains carbon dioxide, the latter must first be removed by means of dilute sulphuric acid.

II. Organic Anions are present.

SEC. 176.

General Survey.

The separation of organic anions depends upon the use of the group reagents: hydrochloric acid, calcium chloride, and ferric chloride.

(*a*) *Hydrochloric acid* precipitates cinnamic acid (practically completely), and partially precipitates benzoic acid and salicylic acid from concentrated solutions. The precipitate is dissolved in sodium hydroxide solution (if necessary after separation of the chlorides of Group V_1 by means of ether. Chap. III., No. 78), and the solution rendered exactly neutral, and separate portions thereof tested with *ferric chloride* as to whether (*b*) a precipitate (cinnamylate ion or benzoate ion), or (*c*) a coloration (salicylate ion) is produced. If the former is the case, a test for cinnamylate ion (*d*) is made with manganous sulphate, and for benzoate ion (*e*) by Mohler's method (Sec. 141, 9), a note being made of what is said on p. 537. (*f*) The filtrate from the hydrochloric acid precipitate (after separation of the cations of Groups II. to VI., and also of silicate and carbonate ion) is treated with *calcium chloride* (*a*) in the presence of ammonia and a sufficient quantity of ammonium chloride. Of the organic anions only oxalic and tartaric acids (with possibly phsophate, etc.) are precipitated, since calcium citrate, malate, and succinate are retained in solution by the ammonium salts (Chap. III., No. 72) (*g*) The precipitated calcium salts may be separated by means of cold sodium hydroxide solution into calcium oxalate, which is insoluble, and calcium tartrate, which dissolves in that reagent. (*h*) The former may be identified by means of manganese dioxide and sulphuric acid (in the presence of calcium phosphate, etc., which may be present). (*i*) Calcium tartrate is precipitated on boiling the sodium hydroxide solution. (*k*) The filtrate from the precipitated calcium salts (*f*) yields, on treatment with three parts of 80 per cent. alcohol, a precipitate of calcium citrate, malate, and succinate, whilst all other organic anions remain in solution. (*l*) If the calcium salts precipitated by alcohol are dissolved in a *little* hydrochloric acid, and the solution treated with excess of ammonia and *boiled*, calcium citrate is precipitated (since there is no longer sufficient ammonium salt present to prevent its precipitation). (*m*) Calcium malate and succinate remain in solution. They may be precipitated again by repeating the treatment with alcohol, and separated from one another and identified by means of the fact that calcium malate is oxidised to calcium oxalate when evaporated with nitric acid. If the residue which has been heated with nitric acid is boiled with sodium carbonate solution, and the liquid filtered from the calcium carbonate, the filtrate will contain the sodium salts in solution. (*n*) The oxalate ion may be precipitated by means of calcium chloride in the presence of ammonium chloride. The filtrate when treated with alcohol (*o*) gives a precipitate of calcium succinate again. On evaporating the alcohol from the first alcoholic precipitation (*k*), and treating the neutral solution with *ferric chloride* (*p*) ferric benzoate is precipitated. (*q*) The solution which has been treated with ferric chloride is violet in the presence of salicylate ion, and red in the presence of acetate and formate ions. With regard to their individual identification when two or three of these anions are present together, *vide infra* (191, 192). This scheme of separating the anions of organic acids may be represented in tabular form (p 662).

Process in detail.

The examination for inorganic anions, which must obviously be made, is carried out as described in Sec. 175.

With regard to the organic anions, conclusions are drawn from the results of the preliminary examinations and of the tests for cations, from the degree of solubility, and from observations during the detection of inorganic anions as to which anions in general can be present, and the subsequent examination is restricted to these.

Thus cinnamylate ion can only be present if hydrochloric acid produced a precipitate in the tests for cations. Tartrate and citrate ions can only be present if both barium chloride and silver nitrate produced a precipitate in the tests for inorganic anions, because barium and silver tartrates and citrates are insoluble in water. In drawing such conclusions, however, it should be noted that they are *only relatively decisive* when considerable quantities of ammonium salts are present, since the salts in question are by no means insoluble under such conditions. See also the statements in Chap. III., No. 72, which are also applicable here.

1. *A portion of the original solution is treated with hydrochloric acid* (*cf.* 102, 104, or 109). **184.**
   - (*a*) *No precipitate is formed.* Cinnamylate ion is absent. The examination is continued at (185).

There may be present the anions of Cinnamic Acid, Oxalic Acid, Tartaric Acid, Citric Acid, Malic Acid, Succinic Acid, Benzoic Acid, Salicylic Acid, Acetic Acid, and Formic Acid.

<table>
<tr>
<td colspan="2" rowspan="2">(*a*) +HCl. Precipitate: Cinnamic acid (benzoic acid, salicylic acid). After separation of any inorganic constituents (by means of ether) the ppt. is dissolved in NaOH solution, and (*b*) a portion of the neutral solution tested with $FeCl_3$.</td>
<td colspan="7">Filtrate (after separation of calories of Groups II and VI): (*f*) $+NH_4Cl + NH_4OH + CaCl_2$.</td>
</tr>
<tr>
<td colspan="2">Precipitate: Calcium oxalate, calcium tartrate; (*g*) treated with NaOH in the cold.</td>
<td colspan="5">Filtrate: Citrate, malate, succinate, benzoate, salicylate, acetate, formate ions. (*k*) + three vols. of 80 per cent. alcohol.</td>
</tr>
<tr>
<td rowspan="3">Precipitate: Ferric cinnamylate, complex ferric benzoate. (*d*) A portion of the NaOH solution (*a*) is exactly neutralised with HCl; $+MnSO_4$. Precipitate: *Manganous Cinnamylate*; (*e*) Another portion of the solution (*a*) is examined by Mohler's test (Sec. 141, 9): Red-brown coloration indicates *Benzoic acid.*</td>
<td rowspan="3">(*c*) Filtrate, violet; *Salicylic acid.*</td>
<td rowspan="3">Residue: calcium oxalate; (*h*) $+MnO_2 + H_2SO_4$. Carbon dioxide indicates *Oxalate ion.*</td>
<td rowspan="3">Filtrate calcium tartrate. (*i*) Boiled. Precipitate. *Tartrate ion.*</td>
<td colspan="3">Precipitate: Calcium citrate, malate succinate, (*l*) Dissolve in a little $HCl + NH_4OH$. boiled.</td>
<td colspan="2">Filtrate: Benzoate, salicylate, acetate, formate ions. Alcohol removed by boiling (*p*) Ferric chloride added to neutral solution.</td>
</tr>
<tr>
<td rowspan="2">Precipitate *Calcium citrate.*</td>
<td colspan="2">Filtrate: Malate, succinate ions; + three vols 80 per cent. alcohol: Precipitate of calcium salts, separated and dried; (*m*) evaporated with HNO_3, boiled with Na_2CO_3 solution, filtered. Solution +HCl, (*n*) $+NH_4OH + CaCl_2$.</td>
<td rowspan="2">Precipitate: Complex *Ferric benzoate.*</td>
<td rowspan="2">(*q*) Filtrate: In presence of salicylate ion (violet); in presence of acetate or formate ions (red). For separate tests of identity, *vide infra* (191). (192).</td>
</tr>
<tr>
<td>Precipitate: Calcium oxalate: *Malate ion.*</td>
<td>Filtrate: Succinate ion (*o*) + three vols of alcohol. Precipitate calcium succinate, (confirmatory test)</td>
</tr>
</table>

(*b*) *A precipitate is formed.* The liquid in which it is distributed is treated with ether (102, *b*).

(α) *The precipitate dissolves completely* (102, *b*, α). The presence of cinnamylate, benzoate, or salicylate ion is indicated. The whole of the solution intended for the detection of organic anions is treated with hydrochloric acid, and the precipitate filtered off, and washed twice with cold water.

The filtrate is treated as in (185), whilst the precipitate is further examined by dissolving it in sodium hydroxide solution, neutralising the solution exactly with hydrochloric acid, and adding *a little neutral ferric chloride solution* to a portion thereof.

(*aa*) *No precipitate is formed.* Cinnamylate and benzoate ions are absent.

The liquid has a violet colour. Salicylate ion is present.

(*bb*) *A precipitate is formed.*

(αα) Another portion of the neutralised sodium hydroxide solution is treated with *manganous sulphate* and allowed to stand for an hour. *If a precipitate is formed, cinnamylate ion* is present. As a confirmatory test a portion of the sodium hydroxide solution is diluted with a large amount of water, and treated with hydrochloric acid.

(ββ) A third portion of the solution in sodium hydroxide is subjected to Mohler's test (Sec. 114, 9) for benzoic acid. A *red-brown coloration* indicates *benzoate ion* (*cf.*, however, p. 537).

(γγ) If the liquid in which ferric chloride produced a precipitate is of a *violet colour, salicylate ion* is present.

(β) *It does not dissolve completely* (102, *b*, β) or (103, α). The ethereal layer, after standing, is separated from the aqueous layer (Chap. III., No. 78), and evaporated, care being taken not to ignite the ether.

(*aa*) *No residue is left.* Cinnamylate ion is absent. The analysis is continued at (185).

(*bb*) *A residue is left.* Cinnamylate, benzoate, or salicylate ion is present.

It is dissolved in sodium hydroxide solution, and the solution treated as described in (*a*). Other organic anions are detected as in (185).

185. *In testing for organic anions*, other than cinnamylate ion, *the liquid must be free from cations of Groups II. to VI.* These are removed (in certain cases after a precipitation with hydrochloric acid) by boiling the solution with sodium carbonate, or, if this does not effect their separation, by precipitation with hydrogen sulphide, ammonium sulphide, and sodium carbonate.

The filtrate from the precipitated metal compounds is acidified with hydrochloric acid, heated, and shaken to remove carbon dioxide and hydrogen sulphide (Chap. III., No. 77). The solution thus obtained is examined as follows :—

2. The liquid is concentrated, and a portion rendered slightly alkaline with ammonia, and treated with ammonium choride and then with calcium chloride in not too small a quantity, the sides of the vessel rubbed with a glass rod, or the vessel vigorously shaken, and the mixture allowed to stand for about two hours.

(*a*) *No precipitate is formed, either immediately or after some time.* Oxalate and tartrate ions are absent. The analysis is continued at (187).

(*b*) *A precipitate is formed immediately or after some time.* It is filtered off and washed, and the filtrate reserved for further examination as in (187). The greater part of the precipitate (which, in addition to calcium oxalate or tartrate, may also be due to calcium phosphate, borate, or fluoride) is treated in the cold with *freshly-prepared* sodium hydroxide solution (free from carbonate) (Chap. III., No. 79), then diluted with a little water, and filtered from any residue (which must eventually be treated as in (186)), and the filtrate boiled for some time. If a precipitate now separates, the presence of tartrate ion may be inferred. It should be filtered off while hot, and examined as in Sec. 134, 11 or 17.

Since the reaction in which calcium tartrate is re-precipitated from its sodium hydroxide solution on boiling may sometimes not be obtained (p. 500, footnote 1), it is necessary, in the event of a negative result, to test the remainder of the precipitate produced by calcium chloride directly with resorcinol and sulphuric acid (Sec. 134, 17). A red coloration indicates the presence of *tartrate ion.*

If the precipitate produced by calcium chloride is not completely soluble in sodium hydroxide solution, it should be tested for oxalate ion, if an examination for that ion has not already been made, by washing it and treating it with dilute sulphuric acid to remove carbonates, and then with manganese dioxide and concentrated sulphuric acid, as in Sec. 110, 10. If an evolution of carbon dioxide is produced, *oxalate ion* is present. **186.**

3. The liquid in which calcium chloride has not produced a precipitate, or the filtrate from such precipitate (in which latter case a little more calcium chloride is added, Chap. III., No. 80), is treated with about three times its volume of 80 per cent. alcohol, and the flask closed, and allowed to stand for some hours at as low a temperature as possible. **187.**

(*a*) *No precipitate is formed.* Citrate, malate, and succinate ions are absent. The analysis is continued at (190).

(*b*) *A precipitate is formed.* The liquid is filtered, and the filtrate treated as in (190), whilst the precipitate is washed with dilute alcohol, and examined as follows [1]:— **188.**

It is distributed in water, a little hydrochloric acid added, the liquid filtered if necessary, and the filtrate rendered strongly alkaline with ammonia, and boiled *for some time* (under certain conditions up to half an hour), during which process the reaction must remain alkaline.

(*a*) *The liquid remains clear.* Citrate ion is absent. Any calcium malate or succinate present is precipitated as in (187) by the addition of three parts by volume of alcohol and allowing the mixture to stand in a closed flask, the precipitate filtered off, washed with dilute alcohol, and separated from the filter, and a portion of it dried in a porcelain basin until all alcohol has been expelled (Chap. III., No. 81). The dry residue is dissolved in nitric acid of sp. gr. 1·35 (about 2 c c.), and the solution evaporated to dryness *on the water bath.* This treatment with nitric acid is *repeated twice more,* whereby malic acid is oxidised to oxalic acid, whilst succinic acid remains unchanged.

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[1] If the amount of the precipitate is very small, it may possibly consist of some residual tartaric acid which has remained in solution after the treatment described in (185). It should, therefore, be dissolved in a little hydrochloric acid, and the process given in (185) and (187) repeated.

The residue finally obtained from the evaporation with nitric acid is boiled for some time with a slight excess of sodium carbonate solution, the solution filtered and a portion of the filtrate *acidified* with acetic acid, and treated with a few drops of calcium chloride solution.[1]

(*aa*) No precipitate is formed. Malate ion is absent. The remainder of the alkaline solution is neutralised exactly with hydrochloric acid, and tested for succinate ion by means of ferric chloride (Sec. 138, 5).

(*bb*) *A precipitate* (of calcium oxalate) *is formed.* The presence of *malate ion* is indicated. Confirmation is obtained by converting the malic acid in the rest of the precipitate (a portion of which was heated with nitric acid, Sec. 137, 2, and p. 520) into fumaric acid. For the detection of succinate ion, the remainder of the alkaline filtrate (α) is acidified with hydrochloric acid, the carbon dioxide expelled, the liquid rendered slightly alkaline with ammonia, and the oxalate ion precipitated from the hot solution by means of calcium chloride. The filtrate is treated with three times its volume of alcohol, and allowed to stand for some hours.

(αα) *No precipitate is formed.* Succinate ion is absent.

(ββ) *A precipitate is formed. Succinate ion* is present. As a confirmatory test, the precipitate is filtered off, washed with dilute alcohol, suspended in water, and treated with dilute sulphuric acid. The liquid is then shaken or subjected to continuous extraction with ether, the ethereal extract separated, and the solvent distilled. By this means *succinic acid* is separated in solid form, and may be identified by dissolving it in sodium hydroxide solution, and adding ferric chloride to the neutralised solution (Sec. 138, 5).

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[1] For other methods of separating malic acid from succinic acid, see Sec. 140.

(β) *A heavy white precipitate is formed. Citrate ion* is present. The liquid is filtered while boiling, and the filtrate tested for malate and succinate ions as in the case of (α). In order to be quite certain that the precipitate consists of calcium citrate, it should be re-dissolved in a little hydrochloric acid, and the solution heated, again rendered alkaline with ammonia and boiled, which must cause the precipitate to be formed again (*cf.* Sec. 136, 3). Stahre's reaction is applied (to the *sulphuric acid* solution) as a confirmatory test Sec. 136, 10). **189.**

4. The filtrate from the precipitate obtained in (188, 3), or the solution which yielded no precipitate on the addition of alcohol (187), is heated to expel the alcohol, neutralised exactly with hydrochloric acid, and treated with a little neutral ferric chloride solution. **190.**

(*a*) *Neither a precipitate nor a coloration is produced.* Salicylate and benzoate ions, and also any considerable amounts of acetate and formate ions, are absent. The analysis is continued at (191) and (192).

(*b*) *A flesh-coloured precipitate is formed. Benzoate ion* is present. As a confirmatory test the precipitate is washed, and treated with a small amount of hydrochloric acid (Sec. 141, 3).

(*c*) *A violet coloration is produced. Salicylate ion* is present. Since the coloration, if pronounced, may mask the presence of a precipitate of complex ferric benzoate, which may be present, the liquid is filtered, and the precipitate washed with water. If a flesh-coloured residue is left, the presence of benzoate ion is indicated, and confirmatory tests should be applied.

(*d*) *A more or less pronounced red coloration is produced.* This indicates the presence of acetate or formate ion in some considerable quantity.[1] The liquid is filtered, and any residue of complex ferric benzoate left on the filter is treated as in (*b*). The filtrate is heated to boiling-point, the resulting precipitate treated with hydrochloric acid, drop by drop, until it just re-dissolves, and the solution diluted with several times its volume of water. *Salicylate ion* may be recognised by the *violet colour* of the liquid.

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[1] Salicylate ion may also produce a red coloration (Sec. 142, 7).

191. 5. For the detection of *acetate ion* either the original *solid* substance is used, or a portion of the *original* aqueous solution (which, if acid, must first be rendered alkaline with sodium hydroxide) is evaporated to dryness for the purpose. A small quantity of this dry substance is treated with a little *alcohol* in a test-tube, an equal volume of *concentrated sulphuric acid* added, and the mixture heated to boiling point. If an odour of *ethyl acetate*, which can usually be recognised most readily when the tube is shaken while the liquid cools or after cooling, *acetate ion* is present (see, however, the paragraph in small type (192) *infra*).

192. 6. Formate ion is detected by rendering a portion of the solution, prepared as in (185), just acid with hydrochloric acid, adding sodium acetate, and heating the liquid with mercuric chloride solution. A white turbidity, due to the separation of mercurous chloride, indicates the presence of *formate ion* (Sec. 143, 6). Confirmatory tests are made with silver nitrate and mercurous nitrate (Sec. 143, 4 and 5).

In the presence of chlorate and chromate ions, acetate and formate ions cannot be detected in the manner described.

If chlorate ion is present, it should be reduced as in Sec. 131, 10, before applying the tests in (191) and (192). In the presence of chromate ion, the original solution is treated with a little sulphuric acid, shaken with an excess of lead oxide, and filtered, and the filtrate treated with sulphuric acid in moderate excess, and distilled. The distillate is neutralised with sodium hydroxide and evaporated nearly to dryness, and the residue tested as in (191) and (192). It is also advisable, when organic acids of the first and second groups are present in any considerable quantity, to distil the liquid which has been treated with sulphuric acid.

MIXED COMPOUNDS.

A. 2. *Substances insoluble in water, but soluble in hydrochloric and nitric acids and in aqua regia.*

Detection of Anions.

General Survey.

Essentially the method of detecting the anions of substances insoluble in water consists in decomposing the compounds in question with alkali carbonate, dissolving the resulting alkali salts in water, and testing the solution for anions as in Secs. 175 and 176. In the case of inorganic substances the decomposition is effected by fusion, and in the case of organic substances by boiling them with alkali carbonate solution.

In exceptional cases where this method presents difficulties special reactions are used for the examination.

Process in detail.

I. In the absence of Organic Anions.

SEC. 177.

In the examination of these compounds all anions, with the exception of chlorate ion, have to be taken into consideration.

Cyanogen compounds and silicates are not examined by this process (*cf.* Secs 180 and 181).

1. *Carbonate*, *sulphide*, *arsenite*, and *arsenate ions*, and also *chromate* **193.**
ion, will already have been detected during the solution of the substance and the examination for cations *Nitrate ion* will have been recognised in the ignition of the substance in a glass tube (8, *cc*).

2. A portion of the substance is mixed with four parts of pure **194.**
sodium and potassium carbonates, and, if a sulphide is present, with a little sodium nitrate, and fused in a platinum crucible in the absence of reducible metal compounds, or in a porcelain crucible if such compounds are present. The cold fused mass is boiled with water (after separation from the crucible as in Sec. 15, p. 60, or in the crucible), the solution filtered, and the filtrate used for the detection of all the anions which may have been in combination with the metals, as described in Sec. 175, with the exception of oxalic acid, which has been destroyed by the fusion (*cf.* Chap. III., No. 82).

If a sulphide was present, a separate portion of the substance is tested for sulphate ion, by heating it with hydrochloric acid, filtering the solution, diluting the filtrate with water, and treating it with barium chloride.

3. Since the phosphates of alkaline earth metals and of aluminium **195**
are only incompletely decomposed when fused with alkali carbonate, it is advisable, when alkaline earth metal ions or aluminium ion are present, and phosphate ion has not yet been detected (*cf.* 160), to dissolve a fresh portion in nitric acid, and to test the solution for *phosphate ion* by means of ammonium molybdate solution (Sec. 107, 10). If a silicate or arsenate is

present, a hydrochloric acid solution is made, silicic acid separated as in Sec. 115, 3, and arsenic by means of hydrogen sulphide, as in Sec. 90, 3, the liquid filtered, the filtrate treated with nitric acid and evaporated nearly to dryness, and the residue diluted with water containing nitric acid, and tested with ammonium molybdate solution.

196. 4. It is also best to test a separate portion for fluorine ion as in Sec. 111, 6 or 7, if alkaline earth ions have been detected in the examination for cations, and fluorine ion has not yet been found (*cf.* 160).

5. A test for *silicate ion* should only be applied to substances which have been treated as in (191), when the fusion was effected in a platinum crucible. If a porcelain crucible was used, a separate test should be applied to the residue obtained by evaporating the hydrochloric or nitric acid solution of the original substance (Sec. 115, 3).

6. For the detection of *oxalate ion* in the absence of organic anions (Sec. 99) a separate portion of the original substance should be boiled with sodium carbonate solution (*cf.* 198). If organic anions are present, a test for oxalate ion should be made. The alkaline filtrate is acidified with acetic acid, and tested with calcium sulphate solution. If a white, pulverulent precipitate is produced, the presence of *oxalate ion* is indicated. As a confirmatory test a portion of the substance is treated as described in Sec. 110, 10, after destroying carbonates, if necessary, by treatment with sulphuric acid alone.

II. In the absence of Organic Anions.

SEC. 178.

197. 1. Tests for inorganic anions are made as described in Sec. 177.

2. For the detection of *acetate ion* the original substance is tested as in Sec. 144, 8, or the distillate obtained after the addition of sulphuric acid is treated with excess of sodium hydroxide and evaporated to dryness, and the residue tested. See also the note in small type (192).

3. A small portion of the substance is mixed with a little dilute hydrochloric acid on a clock-glass. If there is an insoluble residue it should be tested for cinnamylate, benzoate, and salicylate ions as in Sec. 145. Any considerable quantity of the two last may thus be most easily detected, but very minute

quantities may dissolve completely, and it is, therefore, necessary also to take benzoate and salicylate ions into consideration in (198).

4. A portion of the substance is boiled for a few minutes with sodium carbonate solution, to which, if it is not to be concentrated, a little solid sodium carbonate is added, and the liquid diluted and filtered from the precipitate. The whole of the organic anions will now be present, together with sodium ion, in solution. The filtrate is concentrated by evaporation, acidified with hydrochloric acid, and filtered from any precipitated cinnamic, salicylic, or benzoic acid, for which the precipitate is tested as in (184). It is then moderately heated, and repeatedly shaken to expel carbon dioxide, and treated in the same way as the solution prepared by an analogous method in (185). Should the ions of heavy metals or aluminium ion have dissolved (as complex compounds) through the action of organic acids, they must be removed prior to applying the tests for organic acids by the method described at the beginning of Sec. 159. **198.**

MIXED COMPOUNDS.

B. Substances insoluble or dissolving with difficulty in water, hydrochloric and nitric acids, and aqua regia.

Detection of Cations, Anions, and Elements.

SEC. 179.

In this stage of the examination the following substances have to be taken into consideration[1]:— **199.**

Barium, strontium, and *calcium sulphate*,[2] *lead sulphate*[3] and *lead chloride*.[4]

Silver chloride, bromide, iodide, and *cyanide*.[5]

Silicic acid and many *silicates*.

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[1] With regard to the detection of cyanogen compounds insoluble in water or acids, see Sec. 180.

[2] Calcium sulphate is partially dissolved, even by water, and is frequently completely dissolved by acids.

[3] Lead sulphate may be found quantitatively in the solution obtained with acids.

[4] Lead chloride can only be found here if the precipitate insoluble in acids has not been thoroughly washed with hot water.

[5] Silver bromide, iodide, and cyanide are decomposed by boiling with *aqua regia*, and converted into silver chloride. Hence, they can only be found here when a substance is present which is being directly examined as in Sec. 179, owing to its being insoluble in *aqua regia*, or when there is an objection to the preparation of an *aqua regia* solution (see Chap. III., No. 6).

Aluminium oxide of natural occurrence and when strongly ignited, and many aluminates.
Ignited *chromic oxide* and *chromic iron ore* (ferrochromite).
Stannic oxide when ignited and of natural occurrence (tin stone).
Some metaphosphates and arsenates.
Calcium fluoride and some other fluorides.
Sulphur.
Carbon.

Of these substances only those printed in italics are of frequent occurrence. The silicates play so important a part in mineral analysis that they are dealt with separately (Secs. 181 to 184).

General Survey.

Substances insoluble in acids are either combustible or volatile in the air, as *e.g.* the elements carbon and sulphur, or they may be converted by fusion with sodium carbonate (and potassium nitrate) into compounds soluble in water or acids. A fused mass is thus obtained, from which on treatment with water the anions are dissolved, together with alkali ions, whilst the cations are left in a condition in which they can be dissolved by acids.

The cations and anions in these solutions may then be detected as described in the preceding sections. The fusion must be carried out in a platinum crucible, because, if a porcelain crucible is used, its glazing will be attacked, and may yield silicic acid and aluminium to the fused mass.

Substances containing lead, silver, or sulphur, however, must not be fused in a platinum crucible, or it will be attacked; hence, tests for these substances should be made prior to the fusion, and, if present, they must be removed.

In the case of lead compounds, this is effected by extraction with hot sodium acetate solution, whilst silver salts are removed by treatment with hot potassium cyanide solution.

Sulphur is eliminated by ignition.

Since carbon is burned during the fusion, a separate portion of the substance should be tested for this element by heating it in the air.

Process in detail.

The preliminary tests given in (*a*) to (*d*), or (*f*), are applied to the substance which is insoluble or soluble with difficulty in water and acids, if the quantity of substance available permits. Should this not be the case, *only* the test for carbon as in (202, *c*) is made, and the examination at once continued as in (205), but it will then be necessary to take into consideration the possibility of all the substances mentioned at the beginning of this section being present.

(*a*) The physical condition of the substance is noted to determine whether it is uniform throughout, sandy or pulverulent, uniformly coloured, or composed of particles of different colours, etc. A microscope or even a lens is useful for this purpose. **200.**

(*b*) A small portion of the substance is heated in a glass tube fused together at one end. A brown vapour and characteristic sublimate indicates the presence of *sulphur*. **201.**

(*c*) If the substance is black, the presence of *carbon* (charcoal, coal, bone-black, lamp-black, graphite, etc.) is usually indicated. A small portion is heated on platinum foil. If the substance which causes the black colour burns, it was *carbon*. Graphite (easily recognisable by its marking capacity) is only burned completely when oxygen is used and at a strong ignition temperature. **202.**

(*d*) If the substance is of a light colour, a little of it is moistened with ammonium sulphide. If it remains white, lead or silver compounds are not present. The examination is continued at (207). But if it becomes black, or even only darker, it should be tested as in (*e*) and (*f*) (204). **203.**

(*e*) A small portion is heated for some time with a fragment of potassium cyanide and a little water, the liquid filtered, and half of the filtrate acidified with nitric acid, and the other half treated with ammonium sulphide. If the former reagent produced a white precipitate, and the latter (assuming that the amount of potassium cyanide was not too large) a brownish-black precipitate, the presence of *silver* compounds in the substance is proved.

(*f*) If any insoluble residue is left from (*e*), it is thoroughly washed with water, and, if white, is treated with a few drops of ammonium sulphide. If this turns it black, *lead salts* are present. If, however, the residue is already black, it should be heated with a concentrated, slightly acid solution of ammonium acetate,[1] the liquid filtered, and the **204.**

---

[1] This is prepared by treating ammonia solution, undiluted with water, with acetic acid until the liquid shows a faintly acid reaction (Chap. III., No. 83).

filtrate tested for lead ion[1] by means of sulphuric acid and hydrogen sulphide.

205. 1. (*a*) *Lead salts are not present.* The examination is continued at (206).

(*b*) *Lead salts are present.* The substance is heated with a concentrated slightly acid solution of ammonium acetate[1] to about 70°, and the solution filtered, this treatment being repeated until all the lead salt has been extracted (Chap. III., No. 83). A portion of this filtrate is tested for *sulphate ion* with barium chloride, second and third portions for lead ion by the addition of excess of sulphuric acid and of hydrogen sulphide respectively, and the remainder tested for *chlorine ion* by diluting it with 20 parts of water (Chap. III., No. 83, last paragraph), acidifying it with nitric acid, and adding a silver salt solution. Any residue left from the treatment with ammonium acetate is washed, and treated as in (206).

206. 2. (*a*) *Silver salts are not present.* The analysis is continued at (207).

(*b*) *Silver salts are present.* The substance, which was free from lead, or has been freed from lead by extraction with ammonium acetate solution, is repeatedly treated with potassium cyanide and water at a gentle heat (or in the cold if sulphur is present), until all silver has dissolved and has been removed (Chap. III., No. 84). Any residue remaining is washed and treated as in (207), whilst the solution is acidified with nitric acid, after sufficient dilution, *in the open air or in a fume cupboard* (Chap. III., No. 84). The resulting precipitate is filtered off. When washed and fused with sodium carbonate in a hollow on charcoal before the blowpipe, it must yield metallic silver (Sec. 70, 13). Whether the silver was originally in combination with a halogen, and if so, with which, is determined as described in (214). Finally, the liquid filtered from the silver precipitate is tested with barium chloride for sulphate ion.[2]

207. 3. (*a*) *Sulphur is not present.* The examination is continued at (208).

---

[1] The presence of lead in silicates, *e.g.* in lead glass, cannot be detected in this way.

[2] The potassium carbonate frequently present in potassium cyanide may have caused complete or partial decomposition of any sulphates of alkaline earth metals present.

(b) *Sulphur is present.* The substance, which is free from silver and lead, is heated in a covered porcelain crucible [1] until all sulphur has been expelled, and the residue, if any, treated as in (208).

4. A somewhat large portion of the substance, which is free from lead, silver, and sulphur, is heated with two parts of sodium carbonate, two parts of potassium carbonate, and one part of potassium nitrate [2] in a platinum crucible until the mixture is in a state of quiet fusion. The fused mass, which has been separated from the crucible (Sec. 15, p. 56) (or if necessary the crucible and its contents), is placed in a beaker, the mass digested, and then heated with water, and the liquid filtered from the residue which is usually left, and the latter washed until barium chloride ceases to produce a precipitate in the washings (Chap. III., No. 85). (Only the first washing water is allowed to run into the filtrate.) **208.**

(a) *The solution thus obtained* contains the anions of the compounds present in the insoluble residue, and also, under certain conditions, those corresponding to the metals, the hydroxides or oxides of which dissolve as anions in alkali hydroxide solution. The following tests are applied to this solution :— **209.**

(α) A portion is acidified with hydrochloric acid, and tested for *sulphate ion* by means of barium chloride.

(β) Another portion is acidified with nitric acid, and tested with ammonium molybdate solution for *phosphate* and *arsenate ions* (Secs. 107, 10 and 90, 9). If a yellow precipitate is obtained, any arsenate ion present is detected and separated by acidifying a further portion of the solution with sulphuric acid, evaporating it to a small residue on the water bath, and introducing hydrogen sulphide, whilst the filtrate from any precipitate produced is again tested for phosphate ion.

(γ) A portion of the original solution is tested for *fluorine ion* (Sec. 111. 7).

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[1] Sulphur which has escaped detection in (201) will be detected by this means.

[2] The addition of potassium nitrate is also useful in the case of white powders, because it inhibits the injurious influence of any lead silicate present upon the platinum crucible. In the case of black powders the amount of potassium nitrate should be proportionately increased to burn the carbon as completely as possible, but if chrome iron ore is present it is best to omit potassium nitrate.

(δ) If the solution is yellow, *chromate ion* is present. This is confirmed by acidifying another portion with acetic acid, and adding lead acetate.

210. (ε) The remainder of the solution is acidified with hydrochloric acid and evaporated to dryness, and the residue treated with hydrochloric acid and water. If a residue insoluble in boiling water is left, it is *silicon dioxide* (*cf.*, however, Chap. III., No. 87). The hydrochloric acid solution is tested by the usual methods for cations which, owing to their oxides or hydroxides dissolving in alkali hydroxides in a state of fusion, may be found here, especially for *tin* and *aluminium ions*.

211. (*b*) *The residue usually obtained* in (208) is heated with hydrochloric acid (effervescence indicates the presence of carbonates of alkaline earth metals); any insoluble residue should be treated as in (213), and the solution tested for cations as in Sec. 165 (as a rule it is sufficient to apply the tests in Sec. 171).

If much silicon dioxide has been found in (210), it is advisable to evaporate the solution of the residue to dryness, and to treat the mass with hydrochloric acid and water, in order to remove the silicic acid left in the residue as completely as possible. With regard to alkali metal ions which may be present in silicates, see (212).

212. 5. If it has been found that the substance insoluble in acids contains a silicate, a separate portion thereof must be treated as in (228), to determine whether or not the silicate contains alkali metal ions.

213. 6. If a residue is left on treating the substance insoluble in water obtained in (208) with hydrochloric acid, as in (211), it may be either separated silicon dioxide, an undecomposed portion of barium sulphate, or possibly stannic oxide which has remained undissolved; it may also be calcium fluoride, or, if it is of a dark colour, chrome iron ore, since both these compounds decompose only with difficulty when treated as described in (208). We may, therefore, recall the fact that stannic oxide may always be detected as in Sec. 88, 17 or 92, 4, and that calcium fluoride is readily decomposed by sulphuric acid (Sec. 111, 6). In the case of chrome iron ore, however, the decomposition may be easily effected by fusing the *finely powdered substance* with about an equal quantity of sodium peroxide, or by heating it at a clear red heat for $1\frac{1}{2}$ hours with about eight times its weight of a mixture of one part of potassium chlorate and three parts of soda lime. In either case the fused mass will contain the chromium in the form of alkali chromate, which can be extracted with water.

If the residue contains stannic oxide, in addition to chrome iron ore, the former will be left after either of these operations, partly as an alkali stannate in the aqueous extract of the fused mass, and partly as stannic chloride in the solution obtained by treating the insoluble residue from the aqueous extract with hydrochloric acid.

7. If the residue insoluble in acids contains silver (206, *b*), tests have **214.** still to be made as to whether it was present in the original substance as a compound insoluble in acids, or whether it was converted by the treatment into chloride, bromide, iodide, or cyanide (Chap. III., No. 84).

To obtain as complete proof as possible, a portion of the original substance is completely extracted with boiling water and then with nitric acid, the residue washed with water, and a small portion thereof tested for silver ion as in (203) If silver ion is detected the anion with which it is in combination is detected by treating the remainder of the residue with finely granulated zinc and water containing a little sulphuric acid, with frequent shaking, and filtering the liquid after some hours The solution thus obtained may be directly tested for chlorine, bromine, iodine, and cyanogen ions as in Sec. 125. Or the zinc ion may first be precipitated with sodium carbonate, so as to have a solution containing the anions together with sodium ion.

CHAPTER II.

PRACTICAL METHODS FOR SPECIAL CASES.

I. Special process for the examination of cyanides insoluble in water (especially of complex cyanides containing metals in the anion), and also of mixtures which contain such cyanides and are insoluble in water.

SEC. 180.

SINCE, in the treatment of cyanides (especially complex cyanides), insoluble in water, with acids, phenomena may be observed which entirely differ from those appearing with other substances, and which may easily lead to errors; and since some of these complex cyanides are only completely decomposed and dissolved by acids with difficulty, the following process should be used, if the preliminary test (8, *gg* and *ii*) and the behaviour towards acids (33, *g*) point to the presence of these substances.

General Survey.

The object of special treatment in this course is to detect complex cyanogen ions containing metals (such as ferrocyanide, etc.) if they are present, and especially to prevent the metals contained in them from being found among those present as cations.

To attain this object, the substance (if necessary freed from substances soluble in water) should not be treated with acids, which destroy complex cyanides [1] with the evolution of hydrocyanic acid, but should be boiled with sodium hydroxide, and the cations remaining in the residue thus, for the most part, separated from the anions. In the case of many salts, possibly present in admixture, this separation succeeds better if the substance is boiled with sodium *carbonate* instead of with sodium *hydroxide*. The latter is, therefore, added to the former.

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[1] The decomposition with acid is frequently quite incomplete. New substances, also sparingly soluble in acid, are formed, which would offer further difficulties in the examination, as in Sec. 178.

The insoluble residue remaining after this treatment generally contains most of the cations of the original substance in the form of hydroxides and carbonates. It should, therefore, be tested in the ordinary way, beginning with (37).

Since, however, many salts, such as phosphates and fluorides of the alkaline earth metals, are not decomposed with certainty and in any case not completely, even when boiled with sodium carbonate, a portion of this insoluble residue should, according to the result of the test for cations, if necessary be tested for anions as in Sec. 177. The solubility table (Appendix IV.) should be used in deciding whether, and to what extent, this is necessary.

The *alkaline solution* can contain, in addition to the anions originally present, which correspond to the actual acids, the anions of such metals the oxygen compounds of which are electro-negative towards sodium, so that the oxides or hydroxides dissolve in sodium hydroxide solution; that is to say, the members of Group VI (standing on the border line of metals); further, anions containing lead, zinc, aluminium, and also copper and cobalt in small proportion, and (if organic substances which cause the formation of complex ions are present) also complex ions of other metals.

These metals, originally present as cations, must (with the exception of aluminum) be removed from the alkaline solution before testing for anions. This is done by the addition of sodium sulphide, which precipitates the metals of Groups IV. and V., and in the filtrate by the addition of sulphuric acid, or (if no sodium sulphide precipitate is obtained, that is to say, no sodium sulphide is present in the solution) of sulphuric acid and hydrogen sulphide, by which means the members of Group IV. (possibly also mercury, Sec. 71, 4) are separated in the form of sulphides.

Both sulphide precipitates are examined in the ordinary course, it being noted that the first contains the Groups V. and IV., and that these must therefore first be separated in the nitric acid solution of the precipitate before the individual tests are made.

After removing any members of Groups IV., V. and VI. which may be present, the alkaline solution is tested for anions according to Secs. 175 and 176. Since, however, in this course, the only complex cyanogen ions which need be taken into consideration are ferro- and ferricyanogen ions, the cobalticyanogen ion, and also the complex ions containing manganese and chromium would be overlooked. A further portion of the alkaline solution is, therefore, decomposed by heating it with sulphuric acid, and tested for the ions of the above-mentioned metals, as also for that of aluminium (since this, too, may be present in the alkaline solution but not have been detected in the tests already described). Since, among the compounds of complex cyanides insoluble in water some may be present which contain alkalis, as *e.g.* zinc-potassium ferrocyanide, a separate portion should be tested for alkali metal ions after the complex cyanogen ion has been destroyed by heating it with concentrated sulphuric acid (171).

This particular course is represented in the following table :--

<table>
<tr><td colspan="5">There may possibly be present all salts insoluble in water, including those with complex cyanogen ions. (A) Boiled with NaOH and Na_2CO_3.</td></tr>
<tr><td rowspan="4">Residue: Hydroxides and carbonates of cations, salts not decomposed by boiling with Na_2Co_3. The usual tests for cations and organic anions are made beginning at (37)</td><td colspan="4">Filtrate. Na_2PbO_2, Na_2ZnO_2 (and analogous compounds of metals of Groups IV and V.), Sodium salts of members of Group VI., Na_3AlO_3 (sodium salts of complex salts containing organic anions). Sodium salts of anions present in the original substance, including complex metal cyanogen ions. (*a*) + Na_2S.</td></tr>
<tr><td colspan="2">Precipitate. PbS, ZnS and other sulphides of members of Groups IV and V. It is dissolved in HNO_3, + H_2S (1).</td><td colspan="2">Filtrate: Sodium sulpho salts of Group VI (and of mercury). Sodium salts of the original anions, + H_2SO_4.</td></tr>
<tr><td>Precipitate: PbS and other metal sulphides of Group V. Separated as in (125) to (133).</td><td>Solution: $Zn(NO_3)_2$ and other nitrates of Group IV + $(HN_1)_2S$. Precipitate. Group IV separated as in (141) to (149).</td><td>Precipitate: Sulphides of Group VI. (and of Hg) Separated as in Sec 167 (or if Hg is to be taken into consideration, Sec. 166).</td><td>Filtrate. Na salts of the original anions.
(*a*) Examined as in Secs. 175 and 176.
(*β*) Evaporated with H_2SO_4. Heated to expel all HCN, residue dissolved in water, + $(NH_4)OH$ + $(NH_4)_2S$. Precipitate. FeS, CoS, MnS, $Cr(OH)_3$, $Al(OH)_3$ Separated as in Sec. 170.</td></tr>
<tr><td colspan="4">(*b*) + HCl + $BaCl_2$ for sulphate ion. (2)
(*c*) + H_2SO_4 + $FeSO_4$ for ferricyanogen ion. (3)
(*d*) + H_2SO_4 + $FeCl_3$ for ferrocyanogen ion.</td></tr>
<tr><td colspan="5">(B) Heated with H_2SO_4. Residue tested for alkalis (171).</td></tr>
<tr><td colspan="5">(C) A portion of the original substance is tested with HCl for carbonate ion (4)</td></tr>
</table>

Notes to the table: (1) Since as a rule lead ion is the only member of Group **V.** present, the nitric acid solution of the sodium sulphide precipitate may be tested first for lead ion: if found it is separated by evaporation with sulphuric acid, and the filtrate tested for other members of Group V by means of hydrogen sulphide. If the result of the test with sulphuric acid is negative, the solution may be tested directly for members of Group IV. For further details *vide infra*. (2) If sodium sulphide or sulphuric acid have been added to the neutral solution, the latter cannot be used for the detection of sulphate ion. (3) If the solution contains hydrogen sulphide it cannot be tested for ferricyanogen ion, which would then be reduced to ferrocyanogen ion. Hence special tests (*b*), (*c*), and (*d*) must be applied to the first alkaline solution (4) Obviously a test for carbonate ion must not be made upon a portion which has been treated with sodium carbonate.

Process in detail.

215. 1. The substance under examination is freed, if necessary, by treatment with boiling water from all substances which are soluble therein, and a portion of it is boiled with strong potassium or sodium hydroxide solution freshly prepared from solid alkali hydroxide; when it has boiled for a few minutes sodium carbonate is added, the liquid boiled again for some time, the residue (if any) filtered off after dilution of the liquid with water, and then washed.

(*a*) *The residue*, which is now free from cyanogen (it would only contain it if silver cyanide were present), is treated in the ordinary way, beginning at (37). **216.**

(*b*) *The solution* which, if complex cyanogen ions were present (ferrocyanogen ion, cobalticyanogen ion, etc.), will contain them in addition to alkali metal ions, may also contain further anions which were separated from their bases when boiled with the sodium carbonate, and finally such metals in the form of anions, the oxides or hydroxides of which are soluble in alkali hydroxide solution.

(*α*) A small portion is *carefully* treated with hydrogen sulphide water.[1]

(*aa*) *No precipitate or no permanent precipitate is formed.* This indicates the absence of zinc and lead ions and of other metals of the fourth or fifth group (which may have passed into the alkaline solution, possibly through the action of organic substances), with the exception of mercury ion, which can remain in solution, owing to the predominating strongly alkaline reaction, in addition to sulphide ion. The analysis is continued at (217).

(*bb*) *A permanent precipitate is formed.* Sodium sulphide is added, drop by drop, to a fairly large portion of the alkaline solution (216) so long as a precipitate is produced, but as far as possible a considerable excess should be avoided. After gentle heating, the precipitate is filtered off, the filtrate treated according to (217), whilst the washed precipitate is heated with dilute nitric acid, and any residue examined as in (133) for mercuric sulphide and lead sulphate. The nitric acid solution is examined for Groups V. and IV., *either* by treating it with hydrogen sulphide, filtering off any precipitate that may have been formed, and testing it for Group V. according to (125), and testing the filtrate as in Sec. 170, especially (142) to (149), for Group IV.; *or* by first testing the original nitric acid solution according to (126) for lead ion, and, in the event of a positive result, separating this according to (132).

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[1] The addition of hydrogen sulphide water, or the introduction of hydrogen sulphide, until the liquid smells of this reagent (that is to say, until all the hydroxyl ion has been consumed, and, apart from hydrogen sulphide ion, only alkali ion is present in the solution) must, of course, be avoided; otherwise any aluminium ion present, and as well, even sulphides of the sixth group, might be precipitated, which should not occur.

The solution, *free from lead ion*, must now be tested with more hydrogen sulphide for further members of Group V., and, if necessary, these must be separated before they can be examined in accordance with Sec. 170. If, after separation of the lead ion a hydrogen sulphide precipitate is still formed, it should be filtered off, and washed, and then re-dissolved in nitric acid, and tested according to (127) to (131).

217. (β) A small portion of the alkaline liquid in which no precipitate was produced by hydrogen sulphide water, or which was filtered off from that obtained by means of sodium sulphide, is treated with dilute sulphuric acid until the reaction is distinctly acid, and then with hydrogen sulphide, unless the liquid has a strong odour of that reagent.

(*aa*) *Apart from any separated sulphur, no precipitate is formed.* This indicates the absence of members of the sixth group, as well as of any mercury ion contained in this solution. The analysis is continued at (218).

(*bb*) *A precipitate is formed.* A fairly large portion of the liquid mentioned in (217) is treated in the same way as the sample, the resulting precipitate filtered off and washed, and tested for mercury ion and the members of the sixth group as in Sec. 166 or 167. The filtrate is then examined, according to (218).

218. (γ) The liquid, free or freed from metals which are precipitated by sodium sulphide or hydrogen sulphide, should now be tested on the one hand for anions, especially cyanogen ion and complex cyanogen ions, and on the other hand for any metals present in such complex cyanogen ions (iron, cobalt, manganese, chromium) as also for aluminium ion. The following process is used :—

(*aa*) Portions of the liquid are used for testing for anions as in Secs. 175 and 176 The acidified solution should not be boiled for the removal of carbon dioxide or hydrogen sulphide (because the complex cyanogen ions would be decomposed), but these gases should be removed by a rapid current of air. It is, in fact, advisable not to spend too much time on exact neutralisation, but to make the tests for the individual anions as rapidly as possible. If the liquid was already acidified with sulphuric acid, the tests for anions must be made immediately as otherwise any ferro- or ferrihydrocyanic acid would be decomposed. To start with, the acidified solution is tested with ferric chloride for ferrocyanogen ion and with ferrous sulphate for ferricyanogen ion.[1] If the liquid contains hydrogen sulphide, the latter test is, of course, omitted, since ferric hydrogen cyanide is converted by hydrogen sulphide into ferrous hydrogen cyanide. Cobalticyanogen ion may be recognised by the fact that it forms with nickel salts a greenish, and with manganese and zinc salts white precipitates, *the cobalt contained in which may be recognised on fusion with borax.*

(*bb*) A further portion of the liquid mentioned in (218) is evaporated almost to dryness (if necessary after acidification with dilute sulphuric acid), a little pure concentrated sulphuric acid added, and the liquid heated in a fume cupboard until the greater portion of the free sulphuric acid has escaped. The residue is dissolved in water, and a little hydrochloric acid, and tested for iron, manganese, cobalt, chromium, and aluminium ions according to Sec. 170 (141). The detection of the last is only trustworthy, even in the case of a positive reaction, if the potassium or sodium hydroxide solution used in (215) was free from aluminate, that is to say, freshly prepared.

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[1] It should be noted here that ferricyanogen ion originally present may be converted into ferrocyanogen ion, not only by hydrogen sulphide, but also by other substances which have a reducing action, *e.g.* ferrous compounds: $Fe(CN)'''_6 + Fe^{\cdot\cdot} = Fe(CN)''''_6 + Fe^{\cdot\cdot\cdot}$.

219. If metal sulphides had to be precipitated from it, and a test for sulphate ion and ferricyanogen ion in (218, *aa*) was therefore impracticable, further portions of the liquid mentioned in (216) are tested for sulphate ion, after the addition of hydrochloric acid (any lead present having been precipitated by the introduction of carbon dioxide), by means of barium chloride, or, after the addition of nitric acid, by means of barium nitrate, and for ferricyanogen ion [1] by means of ferrous sulphate, with the subsequent addition of hydrochloric acid. If ferricyanogen ion is found here, a sample of the original alkaline solution (216) must also be tested for ferrocyanogen ion by means of ferric chloride and the subsequent addition of hydrochloric acid, because that found in (218) may possibly have been formed only on the reduction of the ferricyanogen ion

2. A further sample of the original substance insoluble in water is decomposed by continuous heating with pure concentrated sulphuric acid, and the residue tested for alkali metal ions (172) after the separation of all other cations.
3. A further portion of the original substance exhausted with water is treated with hydrochloric acid; if a gas is evolved the test for *carbon dioxide* should be made according to Sec. 114, 4.

II. Analysis of Silicates.

SEC. 181.

220. Whether a substance under examination is a silicate or contains a silicate is often determined by the origin of the substance in question, but may also often be inferred from the preliminary test with alkali phosphate (20), or from the behaviour of the substance towards acids (33) and (38).

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[1] *Cf.* Notes 1 and 2 on p. 680

The examination of the silicates differs essentially from the ordinary course only in the preparatory treatment to which it is subjected in order to separate the silicate ion from the cations and to obtain the latter in solution. All the silicates are divided into two classes, which fact must be sharply emphasised here, because it necessitates a different course of procedure. To the first class belong the silicates which are easily decomposed by acids (hydrochloric, nitric, and sulphuric acids), to the second those which are not decomposed, or only with difficulty, by acids. Many minerals are composed of the two kinds of silicates.

In order to determine the class to which a certain silicate belongs, it is very finely powdered, and a portion of it treated with hydrochloric acid at a temperature near boiling-point. If the silicate is not decomposed by the acid, an attempt should be made to decompose a second portion by heating it for some time with a mixture of three parts of pure concentrated sulphuric acid and one part of water. If this also leaves the silicate undecomposed, it belongs to the second division. Whether or not decomposition was effected by the acids may be gathered from the appearance, since a coloured solution is almost always produced, and from the fact that a deposit of gelatinous, flocculent, or fine pulverulent silicic acid takes the place of the original heavy powder, which usually crackles when stirred with a glass rod. To determine whether the decomposition was complete, or if it only affected part of the minerals, the precipitated silicon dioxide is boiled with a solution of sodium carbonate after washing. If it dissolves completely, the decomposition is complete, otherwise it is only partially complete. These preliminary tests afford a means of deciding whether the silicate should be treated according to Secs. 182, 183, or 184.

Before applying further tests a portion of the silicate should be examined, to ascertain whether water is present, by heating it in a quite dry glass tube If the substance contains hygroscopic moisture, it must first be dried continuously at 100°. The portion being tested, which is heated gently at first, is finally ignited vigorously by means of a gas burner provided with a chimney, and thus may be associated with a preliminary test for fluorine ion (Sec. 111, 9).

A. SILICATES DECOMPOSED BY ACIDS.

SEC. 182.

(*a*) *By hydrochloric or nitric acid.*[1]

221. 1. The silicate, finely ground in an agate mortar, is stirred with a little water until it forms a uniform paste, a moderate excess of concentrated hydrochloric (or nitric) acid added, and the mixture heated at a temperature near boiling-point (most conveniently on the water bath) until completely decomposed. A small portion of the liquid is filtered,[2] the remainder, together with the silicon dioxide distributed in it, evaporated to dryness, the residue heated with continuous stirring at a temperature of or only slightly exceeding 100°, until hydrochloric or nitric acid vapours cease or almost cease to escape, allowed to cool, and then moistened with hydrochloric or nitric acid, after which a little water is added, and the whole heated for some time.

By this means silicon dioxide is separated, whilst the cations are dissolved as chlorides or nitrates. The solution is filtered, the residue well washed, and the solution examined in the ordinary way for cations beginning with Sec. 164, II., p. 609, or III. The residual silicon dioxide can never be considered pure without being examined. It often contains some titanium dioxide, occasionally a little barium sulphate, possibly strontium sulphate, and not infrequently a little aluminium hydroxide. It is best tested by repeated heating in a platinum dish with hydrofluoric acid and sulphuric acid until all the silicon dioxide has been removed as silicon fluoride. Finally, the residue is ignited, fused with potassium hydrogen sulphate, and the fused mass treated with cold water. If an insoluble residue remains, it is filtered off, and tested according to Sec. 179 for barium sulphate (and strontium sulphate). The dilute aqueous solution is then tested for titanic acid[3] by means of continuous boiling, or with hydrogen peroxide[1] (Sec. 52, 2 and 9), and the liquid (which either remained clear or was filtered) tested for aluminium ion by means of ammonia. (If there is the possibility that silver chloride separated with the silicon dioxide, a portion should be treated with ammonia solution and filtered, and the filtrate treated with an excess of nitric acid.)

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[1] Nitric acid is preferable to hydrochloric acid, if silver or lead compounds are present.

[2] Any arsenious or arsenite ion present would volatilise if evaporated with hydrochloric acid.

[3] When the silicon dioxide has been separated by evaporation on the water bath, only part of the titanium dioxide will be found in it, the other part (often the greater) is dissolved in the hydrochloric acid solution and precipitated from it, together with the aluminium and ferric ions, by the addition of ammonia solution. To separate this portion, the dried precipitate is fused with potassium hydrogen sulphate, the fused mass dissolved in cold water (tested with hydrogen peroxide), filtered, if necessary, and considerably diluted; hydrogen sulphide is then introduced until all the ferric ion is reconverted into ferrous ion, and the

2. Since other anions often occur in silicates, especially those which are decomposed by hydrochloric acid, the following points should be noted, and the tests applied, in order that they may not be overlooked :—

   (α) *Carbonates* and often *sulphides* may be recognised when treated with hydrochloric acid ; otherwise a test for them should be made according to Sec. 124, 8 or 9. **222.**

   (β) If the separated silicon dioxide is black, becoming white when ignited in the air, *carbon* or *organic substances* are indicated. If the latter are present, the silicates diffuse an empyreumatic odour when heated in a glass tube

   (γ) The portion of the hydrochloric acid solution filtered off before evaporation is tested for sulphate, phosphate, arsenite and arsenate ions ; for the first by means of barium chloride after dilution with water, for the arsenic ions by the introduction of hydrogen sulphide, first in the cold and then at 70° (Sec. 92, 13), and for phosphate ion by means of molybdate solution, after the hydrochloric acid solution has been evaporated almost to dryness on the water bath, with the addition of nitric acid, the residue heated with nitric acid and the solution filtered. If arsenic ions were present, the liquid filtered from the arsenic sulphide can be used in testing for phosphate ion.

   (δ) *Borate ion* is best detected by fusing a portion of the substance with sodium-potassium carbonate in a platinum spoon or crucible, boiling the mass with water, and testing the solution (acidified with hydrochloric acid) with turmeric paper, according to Sec. 109, 5. **223.**

   (ε) *Chlorides* may be extracted from many silicates simply by boiling with water, and detected in the filtrate by means

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liquid boiled for an hour (without filtering off the sulphur), a continuous current of carbon dioxide being meanwhile passed through it. The precipitate is filtered off, washed, and ignited, whereby the separated sulphur burns away and titanium dioxide remains. If it still contains iron, it should be redissolved by fusion with potassium hydrogen sulphate and treatment of the fused mass with cold water, and precipitated by boiling with sodium thiosulphate.

of silver nitrate solution; the most certain method, however, is to prepare a solution of the mineral in dilute nitric acid, and to test this with silver nitrate solution.

(ζ) *Fluorides*, which frequently occur in silicates, sometimes in small, sometimes in fairly large quantities, are detected by the methods given in Sec. 111, 7.

224. 3. If the silicates contain iron, as is generally the case, they must be examined to determine whether it is present in the divalent or trivalent condition, or in both stages of valency. For this purpose a portion of the finely ground substance is heated (as far as possible with the exclusion of air[1]) with moderately concentrated hydrochloric acid, and the liquid diluted, filtered and tested with potassium ferricyanide and with potassium thiocyanate (Sec. 61, 10, and 62, 10).

(*b*) *Silicates decomposed by concentrated sulphuric acid but not by hydrochloric acid.*

225. The very fine powder is heated with a mixture of three parts of pure concentrated sulphuric acid and one part of water (preferably in a platinum dish), the greater portion of the sulphuric acid finally evaporated, the residue heated with hydrochloric acid, diluted and filtered, and the solution dealt with according to Sec. 165; the residue, which, apart from the separated silicon dioxide, may contain sulphates of the alkaline earth metals, is then dealt with as described in Sec. 182, 1, for a residue insoluble in acids. If such silicates are to be tested for anions, a separate portion should be treated according to Sec. 183.

B. SILICATES NOT DECOMPOSED BY ACIDS.[2]

SEC. 183.

226. Since these silicates are most easily decomposed by fusion with sodium potassium carbonate, no test for alkali metals can, of course, be made in portions of the substance thus treated. The whole examination may, therefore, be divided into two main divisions, the first consisting of the detection of silicate ion and all cations, with the exception of alkali metals, and the second of that of alkali metal ions only. A few further tests are necessary to determine the presence or absence of any other anions.

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[1] That is to say, in a boiling flask, through which a current of carbon dioxide is passed, or by mixing a little sodium carbonate or sodium hydrogen carbonate with the powder, and treating it with a sufficient excess of hydrochloric acid in a boiling flask.

[2] This refers to those silicates which are not decomposed when heated with hydrochloric acid and sulphuric acid in *open* vessels (see Sec. 181). If they are heated, however, in the finely powdered condition at 200°–210° with a mixture of three parts of pure concentrated sulphuric acid and one part of water, or with hydrochloric acid in a glass tube closed by fusion, most of them are decomposed, and can thus be analysed by this method (Al. Mitscherlich).

1. *Detection of silicate ion and of all cations with the exception of the ions of the alkali metals*

The very fine powder is mixed with four parts of sodium potassium carbonate, and the mixture fused in a platinum crucible over a gas lamp until the mass is in a quiet state of fusion. The fused mass is removed from the crucible, if possible, in the manner described in Sec. 58, p. 223. If this is successful, the mass is ground up and a portion reserved for the test for anions (230). The portion which is to be tested for cations, or the whole crucible with the fused mass, is covered with water in a porcelain dish, heated for some time until the fused mass breaks up (if a portion of the fused mass has not previously been removed, part of the aqueous solution, together with portions of the mass, is decanted for the purpose of testing for anions), hydrochloric acid added (if necessary also to the residue), and the whole heated until the mass, with the exception of the silicic acid, which separates in flakes, is dissolved. If necessary, the crucible is taken out of the dish, the contents evaporated to dryness, and the residue treated exactly as in the case of that obtained in (221). **227.**

2. *Detection of alkali metal ions.*

For this purpose the silicate must be decomposed with the aid of a substance free from alkali. Hydrofluoric acid is the most suitable, but the same result may be obtained by heating the substance with ammonium chloride and calcium carbonate. **228.**

(*a*) *Decomposition by aqueous hydrofluoric acid.* The finely powdered substance is stirred with water in a platinum dish until it forms a thin paste, hydrochloric acid and aqueous hydrofluoric acid added, and the mixture heated on the water bath while being stirred from time to time with platinum wire (carefully and in the open, in order to avoid breathing or coming into contact with the vapour) until the silicate is dissolved. Dilute sulphuric acid is then added, and the whole evaporated, finally over a naked flame, until the hydrochloric acid, silicohydrofluoric acid, and hydrofluoric acid have completely escaped, and only a small portion of the sulphuric acid remains. When cool, the mixture is diluted with water, heated to boiling point, barium chloride added in slight excess, and then milk of lime, until the reaction is alkaline. After again being boiled the liquid is filtered, treated with ammonium carbonate and a little ammonia, so long as a precipitate is formed, filtered after an hour, and tested for potassium and sodium as described in the case of the corresponding filtrate in (170); it should be tested for lithium, cæsium, and rubidion ions as in Sec. 32, p. 132.

229. (*b*) *Decomposition with calcium carbonate and ammonium chloride* One part of the finely ground powder is mixed with one part of ammonium chloride and eight parts of calcium carbonate, the mixture heated, at first moderately, then more strongly, in a platinum crucible, the residue from the ignition treated with hot water, the liquid filtered, the filtrate treated with ammonium carbonate and ammonia solution, and the examination continued as in (*a*) (J. L. Smith, *Zeitsch anal. Chem.*, **11**, 85).

3. *Detection of fluorine, chlorine, borate, phosphate, arsenite, arsenate, and sulphate ions.*

230. The portion of the fused mass reserved in (227) or its aqueous solution is used, the former being boiled with water and, in either case, the solution, which contains all the anions in solution (including at all events part of the phosphate ion) filtered, and the filtrate tested as follows :—

(*a*) A small portion is acidified with nitric acid, and tested for *chlorine ion* by means of silver nitrate.

(*b*) A second portion is tested for *borate ion* according to Sec. 109, 5.

(*c*) A third portion is treated as in Sec. 111, 8, for the detection of *fluorine ion*.

(*d*) The remainder is acidified with hydrochloric acid, a small portion tested for *sulphate ion* by means of barium chloride, and the rest tested, first in the cold and then at 70° for *arsenic ions*, by means of hydrogen sulphide (Sec. 92, 13). If no precipitate is produced, the liquid is immediately evaporated almost to dryness; otherwise after filtration, with the addition of nitric acid, the residue treated with nitric acid and water, and the solution tested for phosphate ion by means of a solution of ammonium molybdate in nitric acid (Sec. 107, 10).

C. SILICATES PARTLY DECOMPOSED BY ACIDS.

SEC. 184.

The greater number of minerals occurring in nature consist of mixtures of several silicates, one of which is often decomposable by acids, the other not. If these had to be treated in the same way as those completely insoluble, all the elements would be found which are contained in the mineral, but no further information as to the actual composition of the mineral would be obtained. **231.**

It is, therefore, advisable to examine separately those portions of the mixture which show a different behaviour towards acids. For this purpose, the very finely powdered mineral is treated with moderately concentrated hydrochloric acid for some time at a gentle heat, part of the solution filtered, the greater part of the remainder evaporated to dryness with the residue, the mass heated at a temperature of, or only slightly exceeding, 100°, with continual stirring, until little, if any, hydrochloric acid vapours escape, the cooled residue moistened with hydrochloric acid, heated with water, and the liquid filtered.

This solution, which contains the cations of those constituents decomposable by hydrochloric acid, is examined according to (221), the first filtrate according to (222,γ), portions of the original substance according to (222,α and β), and (223) for other acids, and also according to (224) for the degree of valency in which any iron found is present. The residue, which contains the undecomposable portions of the mixture, in addition to the silicon dioxide separated from the decomposed silicate, is boiled with excess of a solution of sodium carbonate, filtered while hot, and the precipitate washed first with a hot solution of sodium carbonate, and then thoroughly with boiling water. The still undecomposed constituents, which have thus been freed from the separated silicon dioxide, are next treated as in Sec. 183. The alkaline liquid, however, is acidified with hydrochloric acid, evaporated to dryness, the residue treated with hydrochloric acid and water, the silicon dioxide filtered off, the filtrate rendered alkaline with ammonia and heated. If a precipitate is formed, this, as also the separated silicon dioxide, should be tested for titanium dioxide as in (221). If there is no reason for separately precipitating the silicon dioxide of the portion decomposed by acids, the tedious treatment with sodium carbonate may be dispensed with, and the residue containing the former be directly decomposed by fusion.

III. ANALYSIS OF NATURAL WATERS.

SEC. 185.

232. The examination of natural waters by analytical methods is simpler, because the substances and compounds which are generally to be found in them are known. Although, strictly speaking, the true nature of a water is indicated only by means of quantitative analysis, in that the main differences between waters lie in the different proportions of their individual constituents, yet qualitative analysis may frequently be of great value, especially when it is noted whether a reagent causes a faint or a strong turbidity, or produces a slight or a voluminous precipitate, since by this means an approximate estimation of the quantitative proportions of the constituents becomes possible. We confine ourselves in the following directions to the actual qualitative chemical analysis, and refrain from giving any particulars regarding bacteriological examinations or quantitative tests. With regard to the latter, reference may be made to R. Fresenius' *Anleitung zur quantitativen chemischen Analyse,* where more information is given concerning the importance of qualitative reactions in combination with quantitative tests.

In the following sections the examination of ordinary water (spring, well, brook, river water, etc.) is distinguished from that of mineral waters (among which sea-water may be included), because the analytical examination of the former is very much simpler than that of mineral water, since far fewer substances have to be taken into consideration.

A. EXAMINATION OF ORDINARY WATER (SPRING, WELL, BROOK, RIVER WATER, ETC.).

SEC. 186.

233. Experience has shown that the following are the substances which have to be taken into consideration in the examination of ordinary water :—

(*a*) *Cations:* Calcium, magnesium, sodium, potassium, ammonium, ferrous ion, manganous ion (possibly derived from the supply pipes : lead ion, copper ion, zinc ion).

(*b*) *Anions:* Sulphate, carbonate, chlorine, silicate, nitrate, nitrite, phosphate, and sulphide ions.

(*c*) Organic substances.

(*d*) Suspended substances, clay, etc.,

This does not mean that no other substances can be present in fresh water; many such are, indeed, to be found, as may be inferred from the origin of springs and proved by analytical examination.[1] They are present, however, in such small quantities that, if litres and not hundreds of litres are being dealt with, they will probably not be detected at all. The method for their detection is, therefore, omitted here, and in regard to them, as also to the oxygen and nitrogen always present in fresh water, reference should be made to the respective chapters in R. Fresenius' *Anleitung zur quantitativen chemischen Analyse.*

I. *The water under examination is clear.*[2]

1. One litre of water collected in a clean vessel (or two litres of water poor in dissolved substances) is acidified with hydrochloric acid, a large excess being avoided. It may occasionally be noticed here that bubbles of carbon dioxide escape, which originate from hydrogen carbonate ion or carbonate ion present in the water. The acidified water is evaporated to dryness in a porcelain dish, the remaining residue again moistened with hydrochloric acid, and heated with continuous stirring at a temperature not, or only slightly, exceeding 100°, preferably on the water bath, until scarcely any odour of hydrochloric acid is noticeable. It is allowed to cool, moistened with strong hydrochloric acid, subsequently treated with a little water, and the whole heated and filtered through a small filter. The insoluble portion must be well washed, since, under certain conditions, it may contain much calcium sulphate, which dissolves with great difficulty. It is advisable to moisten it again on the filter paper with hydrochloric acid of sp. gr. 1·12, and then to wash it with more boiling water. If silicon dioxide **234.**

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[1] Chatin (*J. d. Pharm. et Chim.*, 3rd Ser., **27**, 418) found iodine in all fresh-water plants, but could not trace it in land plants; consequently the water in rivers, brooks, ponds, etc., must contain traces of iodine ion, even though extremely minute. According to Marchand (*Compt. rend.*, **31**, 495), all natural waters contain iodine, bromine, and lithium ions. Van Ankum found iodine ion in nearly all drinking waters in Holland. It might be said with the same certainty that all or most natural waters contain the ions of strontium, barium, fluorine, etc.

[2] Samples of clear water often become turbid if kept for some time, because ferrous ion and manganous ion separate as ferric hydroxide and manganese dioxide hydrate, owing to the oxidising action of atmospheric oxygen, and further, because calcium carbonate may separate in crystalline form, owing to the decomposition of hydrogen carbonate ion. Samples of water should, therefore, be examined as soon as possible after being collected.

now remains on the filter paper (confirmatory test: fumes of hydrofluoric acid), the water contains *silicic acid.*

235. The filtrate is added to the first washings (the later washings being thrown away). The liquid (about 150 c.c.) is now used for the following tests:—

(α) About 10 c.c. are shaken in a test-tube (rinsed with hydrochloric acid free from iron) with a few drops of a 3 per cent. hydrogen peroxide solution and tested for ferric ion by means of potassium thiocyanate.[1] It should be noted that a positive result of the reaction only leads to the conclusion that iron ions are present in the water, but does not determine their degree of valency. As a rule, it may be assumed that in water which does not show an acid reaction towards methyl orange, iron can only be present from the beginning as *ferrous ion.*

(β) About 20 c.c. are tested for *sulphate ion* by means of barium chloride.

(γ) About 50 c.c. are evaporated with nitric acid until a few c.c. remain, and tested with molybdate solution for *phosphate ion* (Sec. 107, 10). It is best to allow the water to stand with the reagent for 24 hours at the ordinary temperature.

(δ) The remainder is treated with ammonium chloride, rendered alkaline with ammonia solution, and filtered from any precipitate produced. The filtrate is treated with ammonium oxalate, and allowed to stand for some time in a warm place. A precipitate indicates *calcium oxalate.* This is filtered off, and the liquid tested as follows:—

  (*aa*) A small portion of the filtrate is tested for *magnesium ion* by means of ammonia solution and sodium ammonium hydrogen phosphate.[2]

  (*bb*) The remainder of the filtrate is evaporated to dryness and ignited, any magnesium ion present separated according to (170), and tests applied according to (171) for *potassium* and *sodium ions.*

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[1] If the test for ferric ion is to be decisive, it is necessary to be certain that the water has not been contaminated during evaporation by impurities such as dust, etc., which may contain iron. It is best to evaporate a separate portion of the water in a retort or a flask with the addition of a few drops of pure hydrochloric acid and one drop of nitric acid, until only a small residue is left, and to test this, as soon as cool, with potassium thiocyanate.

[2] Very small quantities of magnesium ion are detected with certainty if, before the test, the ammonium salts are volatilised, the residue dissolved in dilute hydrochloric acid, the solution treated with ammonia solution, and sodium ammonium hydrogen phosphate added.

2. A fresh sample of water (about 50 c.c.) is treated with nitric acid, and silver nitrate added. A white precipitate or turbidity indicates *chlorine ion.* **236.**

3. In testing for *nitrate ion,* one of the reactions mentioned in Sec. 130, 7 to 12, may be used. The most suitable reaction is that described in 10, applied by carefully mixing the solution of diphenylamine in concentrated sulphuric acid with a little (about $\frac{1}{10}$ volume) of distilled water, and pouring on to it the water, previously treated with a few drops of sodium chloride solution. In the presence of nitrate ion a deep blue ring is formed. In the presence of nitrite ion (see 4) the above-mentioned reactions (except under certain conditions, Sec. 130, 11) are not decisive by themselves as to the presence of nitrate ion, since nitrites give the same reactions In this case the zinc iodide starch reaction described in 4 is applied firstly at once, and then after the reduction of the water (acidified with sulphuric acid) by means of zinc (Sec. 130, 14) If, in the latter case, a stronger blue coloration appears than in the former, the presence of nitrate ion is proved (*cf.* also *Zeitsch. anal. Chem.,* 49, 380).

4. Fresh samples of water are tested for *nitrite ion* according to Sec. 126, either by means of the sulphanilic acid-α-naphthylamine reagent or with zinc iodide starch solution. In the latter case, a sample of the water (about 50 c.c) is treated with about one c.c. of dilute sulphuric acid and about one c.c. of potassium iodide or zinc iodide starch solution (*cf.* p. 486). If a blue coloration appears at once or after a short time, a comparatively large quantity of nitrate ion is present; if the coloration only appears after long standing, the amount of nitrite ion present is small. Access of daylight, and especially of direct sunlight, should be avoided, as this may cause a blue coloration to appear even when no nitrite ion is present. For the sake of certainty, it is always well to make a blank test with the same reagents and a sample of water quite free from nitrite ion. To increase the sensitiveness of the reaction, or when substances are present which influence a direct test in the manner described (for instance, in the case of drinking water hydrated manganese dioxide may have such an effect, since under certain conditions when rinsed from deposits in the supply pipes it may be contained in the water in a fine state of division), a fairly large portion of the water (acidified with a little acetic acid) is

distilled and the first fractions of the distillate submitted to the test described (*cf.* Sec. 126, 2). The test for nitrite ion should always be applied to quite fresh samples of water. Samples which have been kept for some time may sometimes show a positive reaction, even when nitrite ion was not an original constituent of the water; in such cases it may have been produced subsequently by the action of bacteria on the nitrate ion.

237. 5. In testing for *ammonium ion* a fresh sample of water (about 300 c.c.) is treated in a glass cylinder, in a place free from ammonia vapours, with two c.c. of a saturated aqueous solution of sodium carbonate and one c.c. of a solution of sodium hydroxide (one part sodium hydroxide and two parts distilled water), the cylinder closed with a glass stopper, shaken, and allowed to stand. One hundred c.c. of the clear liquid is decanted or filtered (through a washed filter) into another cylinder, and one c.c. of Nessler's reagent added (Sec 30, 10). If a yellow coloration, or, on the addition of one more c.c. of Nessler's reagent, perhaps even a reddish-brown turbidity appears, the presence of more or less ammonium ion in the water is thereby indicated. (See also Sec. 30, 10, 11, and 12, p. 128 *et seq.*)

238. 6. Another sample of the freshly collected water is liberally treated with lime water. If a precipitate is formed which, after it has subsided in a closed flask and the supernatant liquid has been decanted, effervesces on treatment with hydrochloric acid, free *carbon dioxide* or *hydrogen carbonate ion*, or both, are present. If free carbon dioxide is present, no permanent precipitate is obtained when a fairly large quantity of the water is treated with only a little lime water (because in this case soluble calcium carbonate is formed).

The behaviour of the water towards methyl orange and phenolphthalein also affords a means of determining whether hydrogen carbonate ion or free carbon dioxide is present. Samples of the water are treated with small quantities of the above-mentioned indicators. If the water shows an alkaline reaction towards methyl orange and an acid reaction towards phenolphthalein, it contains free carbon dioxide, together with hydrogen carbonate ion; if it shows an alkaline reaction towards both indicators, it contains carbonate ion or hydrogen carbonate ion, but no free carbon dioxide; if it shows an acid reaction towards both indicators, it cannot contain hydrogen carbonate ion, but must contain a free acid which is stronger than carbonic acid.

7. In testing water for *manganous ion*, about 100 c.c. are treated with nitric acid and a slight excess of silver nitrate, and also with five c.c. of 6 per cent. ammonium persulphate solution, and, without the silver chloride being filtered off, heated for a quarter of an hour until it gently boils In the presence of manganous ion, a red coloration of permanganate ion is produced, and also, when large quantities of manganous ion are present, a permanent deposit of hydrated manganese dioxide, which is stable even when boiled (Sec. 58, 7). **239.**

8 In order that any lead, zinc, or copper ion present may not be overlooked (these may be present owing to the use of zinc, lead, or copper supply pipes), one to two litres of the water are acidified with hydrochloric acid, protected from impurities,[1] and concentrated to about 100 c.c., preferably in a retort with a tubulure, the open delivery tube of which is inclined upwards at an angle; the liquid is filtered, if necessary, and treated with hydrogen sulphide. Since some of the lead ion present may also be found in any precipitate which has been filtered off, the latter should be heated with a solution of ammonium acetate, the liquid filtered, and the filtrate tested for lead ion by means of hydrogen sulphide.

If, on treating the first solution with hydrogen sulphide, a black precipitate is obtained, it should be examined according to Sec. 168 for lead and copper ions.

The liquid filtered from such black precipitate, or in which no such precipitate was formed, is boiled until all the hydrogen sulphide is expelled, boiled again after the addition of a little nitric acid, treated when cool with an excess of ammonia, filtered from any precipitate (ferric hydroxide, etc.) which may have formed, and the filtrate treated with ammonium sulphide. If a white precipitate is formed, it indicates the presence of zinc ion.

9 In testing for *organic substances*, it is sufficient in the qualitative examination of water if, as a rule, 200 c.c. are evaporated to dryness, and the residue heated at a gradually increasing temperature. Organic substances may then be detected by the brown or black coloration. If the liquid was not too strongly heated, carbon dioxide, which still has an empyreumatic odour, is as a rule evolved when the residue, which generally contains **240.**

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[1] Such impurities may be caused by the use of brass burners or copper water baths.

carbonates, is treated with dilute hydrochloric acid. To obtain decisive results from this test, the evaporation and heating must be carried out in a glass flask or a retort.[1]

10. *Substances which emit an odour* (putrifying organic substances) are best detected when a flask is two-thirds filled with water, closed with the hand, shaken, and the odour noted; if the odour is that of *hydrogen sulphide*, a test should be made according to (246). The presence of other organic substances which have an odour may be recognised by adding a little copper sulphate to the water before noting the odour.

241. 11. About 500 c.c. are evaporated until a quite small residue is left and the reaction of the liquid tested. If it is *alkaline* and a drop of the concentrated, clear, filtered solution effervesces when mixed on a clock-glass with a drop of acid, and if, on the cautious addition of calcium chloride to the alkaline solution, calcium carbonate is precipitated, the water is "alkaline" (in the narrower sense of the term), *i.e.* the concentration equivalent of the hydrogen carbonate or carbonate ion is greater than that of the alkaline earth ions.

II. *The water under examination is turbid.*

242. 1. A large glass flask is filled with the water, stoppered, and allowed to stand in the dark and in the cold until the water becomes clear; and the clear water is drawn off by means of a syphon and tested as in I., 1, 2, 6, 7, and 9.

2. In testing for ammonium ion (I., 5), nitrate ion (I., 3), nitrite ion I., 4), organic substances with an odour (I., 10), and lead, zinc, and copper ions (I., 8), fresh samples of the turbid water are used, and in tests for nitrite ion the distillation method or the use of sulphanylic acid-α-naphthylamine reagent is generally most suitable for the purpose.

3. If the substances which render the water turbid are to be detected, the deposit which subsides during clarification of the water in the flask (II., 1) is filtered off, and the precipitate remaining on the filter examined. As this may consist of the finest sediment of various minerals, it is first treated with dilute hydrochloric acid; the portion insoluble in the acid is, however, examined as

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[1] With regard to a more exact test for organic substances, see R. Fresenius, *Anleitung zur quantitativen Analyse.*

described in the case of silicates (Secs. 181 *et seq.*).[1] It should be noted that in the case of not quite fresh samples of water, ferrous, manganous, and phosphate ions may already have separated in a flocculent form. They will not be detected by the method described in II., 1, but should be looked for in the hydrochloric acid extract of the deposit.

B. EXAMINATION OF MINERAL WATERS.

SEC. 187.

In the examination of mineral waters the number of constituents 24 which have to be taken into consideration is considerably increased, and the following are those to which the test should, as a rule, be extended :—

The ions of *cæsium, rubidium, thallium, lithium, barium, strontium, aluminium,* as also *borate, titanate, bromine, iodine,* and *fluorine ions, hydrogen sulphide* (*thiosulphate ion, formate ion, propionate ion,* etc., *nitrogen, oxygen, methane*).[2] Further, the ooze-like ferruginous deposit or solid incrustations separated from springs, and also the residue from the evaporation of large quantities of water, should be examined for *arsenite* and *arsenate ions*, as well as for the ions of *antimony, copper, lead, zinc, cobalt, nickel,* and other heavy metals, sufficient care being taken in testing whether these are actually derived from the water and not from metal pipes, taps, etc.[3] The greatest care should also be taken in testing the reagents which are to be used in such delicate examinations.

1. Examination of the Water.

(*a*) *Operations at the spring.*

SEC. 188.

1. The water is filtered at the spring (if it is not already absolutely 244 clear) through washed filter paper (p. 38) into large flasks closed with glass stoppers. The precipitate remaining on the

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[1] With regard to the more exact examination, see R. Fresenius, *Anleitung zur quantitativen chemischen Analyse.*

[2] With regard to the constituents given in brackets, reference should be made to the corresponding chapters in R. Fresenius, *Anleitung zur quantitativen chemischen Analyse,* since detection and quantitative determination are usually combined.

[3] In this respect, as in fact in regard to the whole analysis of mineral waters, see the numerous analyses of mineral waters published by the Fresenius' Chemical Laboratory.

filter, and which, apart from flocculent matter suspended in the water, may possibly contain constituents which separate at once on contact with air (ferric hydroxide, ferric phosphate, ferric silicate, ferric arsenate), is examined for these substances as described below in Sec. 190.

245. 2. The water need scarcely be tested for *free carbon dioxide*, as its presence may be seen with the naked eye. If actual reactions are required, however, the water may first be tested with solutions of methyl orange and phenolphthalein, *cf.* (238), and then with lime water; the latter produces a turbidity which should disappear on the addition of an excess of the mineral water.

246. 3. A test for *free hydrogen sulphide* and *hydrogen sulphide ion* [1] is then made by noting the odour. For this purpose a flask is half-filled with mineral water, closed with the hand, shaken, and the odour noted. In this way distinct traces are often found which can hardly be detected by reagents. If visible reactions are required, an alkaline lead solution or, if a voluminous white precipitate is thereby formed, an aqueous solution of cupric chloride, is introduced drop by drop into the large white flask filled with the mineral water, the flask placed on a white surface and, when viewed from above, note taken whether the water assumes a brownish coloration or gives a blackish precipitate. Another sensitive test, which depends on the formation of methylene blue, is as follows: The water under examination is treated with $\frac{1}{50}$ volume of fuming hydrochloric acid, a few crystals of para-aminodimethylaniline sulphate added, and, as soon as this has dissolved, one to two drops of a dilute ferric chloride solution introduced. In the presence of hydrogen sulphide the liquid (which would otherwise be light red) becomes pure blue after some time (H. Caro, E. Fischer) (see Sec. 124, 6).

If the presence of hydrogen sulphide in an alkaline mineral water cannot be detected unmistakably by its odour, the following test should be applied: A large flask, half filled with the water, is closed by means of a cork, to the middle of which a strip of paper soaked in lead acetate solution and then moistened with ammonium carbonate solution is attached, and note taken whether this turns brown in the course of several hours. The flask should be shaken slightly from time to time.

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[1] A qualitative analytical separation of the two constituents is not possible; it can only be calculated on the basis of the equilibrium between the free hydrogen sulphide, hydrogen sulphide ion, free carbon dioxide, and hydrogen carbonate ion. *Cf.* Fr. Auerbach, *Zeitsch. physikal. Chem.*, **49**, 27, (904)

4. A fairly large sample of the mineral water is treated with a little tannic acid, and another portion with a little gallic acid. If a reddish-violet coloration appears in the former case, and a bluish-violet in the latter, *ferrous ion* is present. The colorations only appear after some time, and, owing to the action of air, darken from the top of the liquid downwards. The water should be tested for ferric ion, which is occasionally present, by means of potassium thiocyanate, after the addition of hydrochloric acid. **24**

5. Tests for *nitrite ion* and *organic substances which have an odour* are made according to (236) and (240). If the water contains hydrogen sulphide, this should be removed, before testing for nitrite ion, by the addition of a little freshly precipitated and washed lead carbonate, and the liquid filtered. **24**

(*b*) *Operations in the laboratory.*

SEC. 189.

Since, in qualitative examinations, it is desirable to form an estimate of the proportions in which the individual constituents are present in the water, a small portion of the sample is used to detect the main ingredients, and as far as practicable to determine their proportions, and consequently the character of the water; a larger portion is used for the detection of the ingredients in small quantity, and finally a considerable volume (or the incrustations) used for the detection of exceedingly small quantities.

If the water under examination does not flow clear from the spring, it must be filtered immediately it is collected, since the suspended substances do not have to be taken into consideration in the analysis of water. If such a filtered sample becomes turbid again before the examination can be commenced, these later deposits should not be removed. They should, as far as possible, be distributed, by shaking, throughout the water before the separate portions are measured off for the different tests. In such a case it is still better to use the whole contents of the flask.

1. Method of detecting the Constituents present in Large Quantity.

(*a*) One to 1·5 litres of mineral water are acidified with hydrochloric acid, evaporated, and tested as in (234) and (235) for *silicic acid, sulphate ion, calcium ion, magnesium ion, potassium ion,* and *sodium ion.* **249.**

(*b*) Other portions of the water are tested as in (236) for *chlorine* and *nitrate ions*. In this particular instance any subsequent turbidities should be filtered off. Further, the water should be tested for its alkalinity in the restricted sense as in (241).

(*c*) The tests for *ammonium ion* and *organic substances* are made by means of the methods described in Sec. 186. If, for any particular reason, the water is not suitable for a direct test for ammonium ion according to (237), it should be distilled with the addition of a little freshly boiled potassium or sodium hydroxide solution, and the distillate tested. It may be again pointed out here that the ammonium reaction does not take place with Nessler's reagent if the liquid contains free carbon dioxide, hydrogen carbonates, or sulphides of the alkali metals (*cf.* p. 129).

2. Method of detecting the Non-volatile Constituents present in Small Quantity.

250. A portion of the water (at least 10 litres) is evaporated to dryness in a platinum, silver, or porcelain dish in a place as free as possible from dust and under the cleanest conditions. If the water is not "alkaline" in the restricted sense (241), pure potassium carbonate is added until it is slightly in excess. The evaporation may at first be carried out over a free gas flame, but finally a sand bath should be used. The dry mass is very gently ignited. If it is in a platinum or silver dish, the ignition can be completed in them. If, on the other hand, it is in a porcelain dish, the contents should be transferred into a platinum or silver dish, and then gently ignited. If the mass becomes black on ignition, this is an indication that organic substances were present in the water.[1]

The residue thus obtained is evenly mixed and divided into three parts, *a*, *b* and *c*, *c* consisting of half, and *a* and *b* each of a quarter of the quantity.

251. (*a*) *Test for phosphate ion.* The portion *a* is heated with a little water, pure hydrochloric acid added in sufficient excess, the whole evaporated to dryness on the water bath, the residue again heated with acid, and, after slight dilution, the liquid filtered through a filter paper washed with hydrochloric acid and water; the solution is evaporated (finally with the repeated addition of nitric acid) to a small residue, and then tested for *phosphate ion* by means of a nitric acid solution of ammonium molybdate (Sec. 107, 10).

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[1] This conclusion is only correct if the water was effectively protected from dust during evaporation; if this was not the case, and it is desired to determine the presence of organic substances with certainty, a separate portion of the water should be evaporated in a retort.

252. (*b*) *Test for fluorine ion.* The portion *b* is heated with water, calcium chloride added so long as a precipitate is formed, the liquid allowed to stand, and the precipitate, which consists mainly of calcium carbonate and magnesium carbonate, filtered off. When washed and dried it is ignited, treated in a small dish with water, acetic acid added in slight excess, the whole evaporated to dryness on the water bath, heated until all odour of acetic acid has disappeared, and, after the addition of water, again heated; the solution of the alkaline earth metals is filtered, and the residue washed, dried, or ignited and tested for *fluorine ion* as in Sec. 111, 7.

253. (*c*) *Tests for the remaining constituents present in small quantity.* The portion *c* is repeatedly boiled with water, the liquid filtered, and the insoluble portion washed with boiling water. There will remain a residue (α) and a solution (β).

(α) The *residue* consists mainly of calcium and magnesium carbonates, silicon dioxide, and (in iron springs) ferric hydroxide. It may also contain small quantities of barium, strontium, and manganous carbonates, aluminium hydroxide, and titanium dioxide, and must therefore be tested for these. It is treated with water in a platinum or porcelain dish, hydrochloric acid added until it is slightly in excess, then four to five drops of dilute sulphuric acid, the mixture evaporated to dryness on the water bath and the residue moistened by the addition of only a slight excess of hydrochloric acid; water is then added, the whole gently heated, filtered, and the residue washed.

254. (*aa*) *Examination of the residue insoluble in hydrochloric acid.* This residue will consist mainly of silicon dioxide, but it may also contain sulphates of the alkaline earth metals, titanium dioxide, and carbon. It is repeatedly heated in a platinum dish with hydrofluoric acid, or ammonium fluoride, with the addition of a little sulphuric acid, until all the silicon dioxide has volatilised. It is finally evaporated to dryness, any residue fused with a little potassium hydrogen sulphate, the fused mass treated with cold water, the liquid filtered, and the solution tested for *titanic acid* by means of hydrogen peroxide, or by continued boiling (Sec. 54, 9 and 2). If an insoluble residue remained on treating the fused mass with water, it should be washed, and the filter paper incinerated. If a spectroscope is available, the ash should be attached to a loop of platinum wire, exposed for a short time to the reduction flame, moistened with hydrochloric acid, and tested spectroscopically for *barium ion ;* strontium ion will not be found here, or only in small traces. If a spectroscope is not available, the ash should be put aside for a while.

255. (*bb*) *Examination of the hydrochloric acid solution.* The solution is treated with a little ammonium chloride in a boiling flask, then with sufficient ammonia solution (free from carbonate) to render the liquid just alkaline, and finally with freshly prepared ammonium sulphide containing no free ammonia. The flask, filled to the neck, is corked and allowed to stand in a warm place for 24 hours. If a precipitate is formed, it should be filtered off, dissolved in hydrochloric acid, the solution boiled, treated with an excess of potassium hydroxide solution free from aluminate, again boiled, filtered and half of the filtrate tested for aluminium ion[1] by the addition of ammonium chloride, whilst the second half is tested for *zinc ion* by the addition of a little hydrogen sulphide water. A portion of the residue is fused with sodium carbonate for the purpose of testing for *manganous ion*, the remainder then tested for *ferric ion* by dissolving it in hydrochloric acid, boiling the solution with a little nitric acid, and treating the cooled and diluted liquid with potassium thiocyanate or potassium ferrocyanide.

If the examination of the precipitate obtained by means of ammonium sulphide is to extend only to zinc ion and manganous ion, it is preferable, in the presence of much ferric ion, to oxidise the solution of the precipitate in hydrochloric acid by boiling it with nitric acid, to precipitate the ferric ion as a basic salt according to

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[1] In testing for aluminium ion, the conclusion that it was present in the water is only justified when the evaporation of the water, etc., was carried out in a dish made of platinum or silver, but not of porcelain, and when it has been proved that it was not derived from the reagents used.

Sec. 63, 3, *b*, to treat the filtrate with sodium acetate, to acidify it with acetic acid, and to precipitate any zinc ion by means of hydrogen sulphide; the filtrate is then tested for manganous ion by means of bromine and ammonia (*cf.* Sec. 63, 4, γ).

The liquid filtered from the ammonium sulphide precipitate may still contain traces of manganous ion and barium ion; all or nearly all the strontium ion will also be found in it. This liquid is first acidified with hydrochloric acid, then concentrated by evaporation, the separated sulphur filtered off, bromine water added until a deep yellow coloration appears, then a slight excess of ammonia added, and the whole boiled for some time. If a slight brown precipitate separates, it will be due to traces of manganous ion, which have not been precipitated by the ammonium sulphide. If necessary, the liquid is filtered, the filtrate treated with ammonium carbonate and ammonia, filtered after standing for some time, and the precipitate washed, dried, and tested by Engelbach's method described on p. 158. The liquid obtained by boiling the ignited precipitate is evaporated to dryness with hydrochloric acid, and the residue spectroscopically examined for *strontium ion* and any traces of *barium ion* present. If a spectroscope is not available, the liquid obtained by boiling the ignited precipitate with water is evaporated to dryness, after the addition of a little hydrochloric acid, the residue dissolved in water, and the solution added to that obtained by fusing the residual ash reserved in (254) with a little sodium carbonate, treating the fused mass with water, washing and dissolving the residue in hydrochloric acid, evaporating the solution to dryness, and dissolving the residue in water. The combined solutions are then tested for barium and strontium ions according to (163).

(β) The alkaline solution contains the alkali ions and generally **256.** some magnesium ion and traces of calcium ion. It should now be tested for *nitrate*,[1] *borate*, *iodine*, *bromine*, and *lithium*

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[1] The nitrate ion may have been destroyed during the gentle ignition of the residue (250) if this contained organic substances. If there is a possibility of this being the case, and no nitrate ion was detected in (249), a larger portion of the non-ignited residue should be tested as in (257).

ions. It is concentrated by evaporation, cooled, the dish inclined so that the small residue of alkali solution still present separates from the crystallised saline mass, one drop of the concentrated solution placed on a clock-glass by means of a glass rod, the liquid rendered just acid with hydrochloric acid, and tested with turmeric paper for *borate ion* (Sec. 109, 5). The whole contents of the dish are now evaporated, with continuous stirring, to a dry powder, which is divided into two parts, *aa* and *bb*. Of these *aa* should consist of two-thirds, and *bb* of one-third.

257. (*aa*) The larger portion is tested for *nitrate, iodine*, and *bromine ion*. The powder is finely ground, boiled three times in a flask, heated in a water bath, with pure 80 per cent. (by weight) alcohol, and the solution filtered each time. The alcoholic extract is treated with a few drops of potassium hydroxide solution, the alcohol distilled to a small residue, and allowed to cool. Any small crystals which separate may consist of potassium nitrate; the liquid is decanted from them, the crystals washed with a little alcohol, and dissolved in a very little water, and the solution tested for *nitrate* ion by means of diphenylamine, brucine, or indigo (Sec. 130). The alcoholic solution is now completely evaporated to dryness. If nitrate ion has not yet been found, a small portion of the residue is dissolved in a quite small quantity of water, and this solution used for the test. The larger portion of the residue (or the whole of it) is treated three times with warm alcohol, the extracts filtered, the filtrate evaporated to dryness, with the addition of one drop of potassium hydroxide solution, and the residue ignited, and dissolved in a very little water. The solution is slightly acidified with sulphuric acid, and a little pure carbon bisulphide added; finally, for the detection of iodine ion, a small drop of a solution of nitrous acid in sulphuric acid, or a very small quantity of potassium nitrite solution is added. After the mixture has been shaken, and note taken whether the carbon bisulphide gives a violet or a reddish coloration, which indicates the presence of *iodine*, the liquid is tested for *bromine ion* by the cautious addition of chlorine water to the

same liquid, according to the method described in Sec. 125, 7.

(*bb*) *The smaller portion is tested for lithium ion.* For this 258 purpose the residue, which must contain any lithium present in the form of carbonate or phosphate, is heated with water, hydrochloric acid added until the reaction is distinctly acid, and the liquid evaporated nearly to dryness and mixed with pure 80 per cent. (by weight) alcohol; in this process the greater portion of the sodium and potassium compounds separate, whilst the whole of the lithium ion passes into the alcoholic solution. The solution is filtered, the alcohol evaporated, and the residue spectroscopically examined for lithium (Sec. 32, III., 7).

If a spectroscope is not available, the residue just mentioned is dissolved in water with the addition of a drop of hydrochloric acid, a little ferric chloride added, and sufficient milk of lime to give a strongly alkaline reaction; the solution is boiled and filtered, the filtrate treated with ammonium carbonate and filtered, and the liquid, now free from phosphate ion and the ions of the alkaline earth metals, evaporated to dryness, the residue gently ignited until ammonium salts have escaped, and then, after the addition of a drop of hydrochloric acid, treated with a mixture of absolute alcohol and anhydrous ether. The solution is filtered, concentrated by evaporation, and finally the alcohol ignited. If it burns with a carmine red flame, lithium ion is present. As a confirmatory test, the substance is converted into lithium phosphate. Before concluding that the residue (left on evaporating the liquid with sodium phosphate and a little sodium hydroxide, and treating the residue with water and ammonia) is lithium phosphate, tests should be made to prove whether it also shows the characteristic properties of that compound (Sec. 32, III., 4).

3. Detection of Constituents present in exceedingly Small Quantity.

About 100 to 150 litres of water are evaporated by degrees in a 259 porcelain dish, or in a large absolutely clean iron basin, until the salts soluble in water begin to separate. If the mineral water is not alkaline in the restricted sense (241), sufficient alkali carbonate is first added to render the reaction towards phenolphthalein distinctly alkaline. After evaporation, the solution is filtered, the precipitate washed, without adding the last washings to the first filtrate, and the examination continued as follows :—

(*a*) The *precipitate* is examined in the manner described in Sec. 190 for incrustations.

(*b*) The *solution* is treated with hydrochloric acid until the reaction is acid, heated, any arsenite or arsenate ion present precipitated by means of hydrogen sulphide (262), any sulphate ion present just precipitated with barium chloride ; the solution is then filtered, the filtrate evaporated to dryness, the residue digested with 80 per cent. (by weight) alcohol, and the solution tested for cæsium ion and rubidium ion as in Sec. 132, last paragraph. The residue insoluble in alcohol is dissolved in water, and the hot concentrated solution treated with a very slight excess of ammonia. If a precipitate is formed, it should be filtered off. The hot solution, filtered if not still clear, which contains but little free ammonia, is treated with potassium iodide ; if a precipitate is formed at once or after some time, it is filtered off, and spectroscopically examined for thallium ion (Sec. 65, 14).

2. EXAMINATION OF INCRUSTATIONS.

Sec. 190.

260. 1. A large quantity (about 50 to 200 grms.) of the ferruginous deposit or incrustation (from which impurities have been picked, sifted, or elutriated, and adsorbed soluble salts have been washed) is digested with water and hydrochloric acid at a quite moderate heat (effervescence indicates carbonate ion) until all soluble matter has dissolved ; it is then diluted, allowed to cool, filtered, and the residue washed.

(*a*) *Examination of the filtrate.*

(*α*) A portion of the filtrate is well diluted, the greater portion of the free acid neutralised with ammonia, and the still absolutely clear liquid treated with barium chloride, and allowed to stand for 12 hours in a warm place. A white precipitate indicates *sulphate iron.*

261. (*β*) The larger portion of the filtrate is heated at 70°, hydrogen sulphide introduced continuously into the liquid, even while it is cooling, and the flask allowed to stand in a fairly warm place until only a faint odour of hydrogen sulphide remains; the liquid is then poured through a filter and set aside for testing as in (264). If the precipitate contains a fairly considerable quantity of sulphur, as is the case if the solution contained much ferric ion, it is thoroughly washed by decantation, the washings being passed through the filter, and triturated with water while still moist. The dough-like mass is washed into a boiling flask, petroleum spirit added, the mixture well and continuously shaken, the liquid transferred as far as possible into a second flask, and the still undissolved residue again shaken with petroleum spirit and water, until the sulphur is completely, or almost completely, removed. If an insoluble residue is left, which may indicate the presence of sulphides, the whole of the liquids should be passed through a moistened filter, on to which the precipitate is also transferred, the water then allowed to drain off, the petroleum spirit decanted from the metal sulphides adhering to the filter, and the moist filter paper spread out in a small porcelain dish, and treated according to (262).

If the precipitate produced by hydrogen sulphide contains but little sulphur, treatment with petroleum spirit is unnecessary. The filter paper containing the well-washed precipitate is laid in the porcelain dish as it is.

The contents of the filter are heated with a little sodium **262.** sulphide solution, diluted, filtered, and the residue washed with water containing a little sodium sulphide. The solution thus obtained is rendered distinctly acid with hydrochloric acid, and shaken vigorously with petroleum spirit. If an insoluble residue is left, it is filtered off on a moistened filter paper, the aqueous solution allowed to drain off, the petroleum spirit decanted, the precipitate adhering to the filter paper washed, the filter paper spread out first on absorbent paper and then in a porcelain dish, and tests made for the members of the sixth group, especially for *arsenic* and *antimony ions*, according to Sec. 92, 2 or by one of the other methods given in Sec. 92.

If a residue remained after treating the hydrogen sul- **263.** phide precipitate with sodium sulphide, it is separated from the filter by means of a jet, after washing, and boiled with a small quantity of dilute nitric acid. If a residue is left, it is filtered off, washed, and the contents of the filter repeatedly treated with a hot solution of ammonium acetate, in order that any lead sulphate present may not be overlooked. This filtrate is then tested for *lead ion* by means of hydrogen sulphide, whilst the contents of the filter, if there were any, are tested for *barium* and *strontium ions* as on p. 158. The nitric acid solution is treated with pure sulphuric acid, evaporated to dryness on the water bath, and tested as in (126) for lead ion, cupric ion, and any other metal ions of the fifth group possibly present.

264. A portion of the filtrate from the hydrogen sulphide precipitate is evaporated almost to dryness on the water bath, with the addition of excess of nitric acid, the residue treated with nitric acid and water, the liquid filtered, and the filtrate tested for *phosphate ion* by means of ammonium molybdate solution.

The remainder of the filtrate from the hydrogen sulphide precipitate is heated with nitric acid until the ferrous ion, which is nearly always present, and often in considerable quantity, has been converted into ferric ion, and the examination continued as in (*aa*) or (*bb*), according to whether the solution contains little or much ferric ion.

(*aa*) *The solution contains but little ferric ion.* The solution is treated with ammonia in slight excess, filtered, the precipitate washed, dissolved in hydrochloric acid, the solution boiled, allowed to cool, again treated with a small excess of ammonia, and once more filtered.

(*αα*) The *precipitate* is dried, powdered, ignited continuously and sufficiently strongly in a current of hydrogen in a little boat introduced into a glass tube, until the ferric oxide present is converted into metallic iron; it is then allowed to cool completely in the current of hydrogen, and the residue treated with dilute nitric acid until the iron present is dissolved. If a residue is still left, it is washed and then fused with potassium hydrogen sulphate, the fused mass treated with cold water, the *silicon dioxide* (which invariably remains) filtered off, and a small portion of the filtrate tested with hydrogen peroxide for *titanic* *acid.* If this acid is present the remainder is boiled continuously to separate the titanium dioxide (Sec. 52, 2). The solution filtered from the silicon dioxide or from the metatitanic acid is tested for *aluminium ion* by heating it with a moderate excess of ammonia. If the resulting precipitate is not white but brownish-red, that is to say, still contains ferric hydroxide, it should be filtered off and washed, and then dissolved in hydrochloric acid, the solution heated with an excess of potassium hydroxide solution free from aluminate, filtered after dilution, and the filtrate tested for aluminium ion by heating it with ammonium chloride, or by acidifying it with hydrochloric acid, and adding ammonia.

(ββ) The *solution* is acidified with acetic acid, treated with ammonium acetate, and then heated with gaseous hydrogen sulphide. If a pure white precipitate is formed, which does not dissolve when shaken with petroleum spirit, the presence of *zinc ion* is indicated; if, on the other hand, a black or blackish precipitate is formed, it should be tested for *cobalt, nickel,* and *zinc ions* as in (142).

Manganous ion (almost invariably present) is precipitated by bromine and ammonia from the filtrate separated from the precipitate produced by hydrogen sulphide in the acetic acid solution (Sec. 58, 7), and the liquid, filtered from the separated hydrated manganese dioxide, is tested for *barium, strontium, calcium,* and *magnesium ion* according to (161) and (167). If they are not all detected here, the hydrated manganese dioxide precipitate, which contains small particles of compounds of the alkaline earth metals, is dissolved by heating it in hydrochloric acid, the manganous ion precipitated with ammonia and ammonium sulphide solution, the liquid filtered, and the filtrate tested as in (161) and (167) for the ions of the alkaline earth metals.

(*bb*) *The solution contains much ferric ion.* In this case the process described in Sec. 63, A, 3, *b*, is used, in order to precipitate the ferric ion as basic salt; the liquid is then filtered, the precipitate washed with water containing ammonium chloride, the filtrate concentrated as far as possible in a platinum dish, allowed to cool, ammonia added in slight excess, the liquid filtered, the precipitate washed, and the first main precipitate united with that obtained on the second precipitation with ammonia solution; this precipitate is dealt with as in (*aa*) (*αα*), and the liquid filtered from the ammonia precipitate as in (*aa*) (*ββ*).

265. (*b*) *Examination of the residue.* This generally consists of sand, hydrated silicon dioxide, clay, and organic substances, but, if hydrogen sulphide is present in the water, may also contain sulphur as well as the sulphates of barium, strontium, and perhaps calcium. It is boiled first for some time with a solution of sodium carbonate and sodium hydroxide to dissolve the silicon dioxide and any sulphur present, the solution diluted and decanted from the residue on to a filter; the residue is boiled twice more with fresh portions of the sodium carbonate solution, and the precipitate transferred to a filter, and washed.

(*α*) *Examination of the solution.* A part of the filtrate first obtained is acidified with hydrochloric acid (an odour of hydrogen sulphide indicates the presence of *sulphur* in the spring deposit), evaporated to dryness, the residue heated with hydrochloric acid, diluted with water, the liquid filtered, and the still undissolved residue washed, dried, and ignited, in order to separate *silicon dioxide* from any sulphur present. Should there be any doubt as to the presence of sulphide ion in the alkaline solution, a portion of it should be tested with alkaline lead solution (Sec. 124, 4).

(*β*) *Examination of the residue.* This is treated with dilute hydrochloric acid to dissolve any barium and strontium ions present which may have been contained in the incrustation as sulphates, and have been converted into carbonates when boiled with sodium carbonate. The hydrochloric acid solution is tested according to (163) for barium and strontium ions, and the residue, insoluble in hydrochloric acid, is examined as in Sec. 183.

2. The test for *fluorine-ion* is best made on a separate portion of the ferruginous deposit or incrustation. If it does not already contain much calcium carbonate, it is mixed with about half its weight of pure calcium hydroxide, ignited (in which operation *organic substances* may also be detected), the residue stirred with water, acetic acid added until the reaction is acid, the mixture evaporated to expel the acetic acid, and then dealt with as in (252). **26**
3. If arsenic ions have been found, the ferruginous deposit or incrustation is boiled continuously with concentrated potassium or sodium hydroxide solution, the liquid filtered, and the filtrate tested according to Sec. 92, 13, to determine whether the arsenic is present in the incrustation in the form of arsenite or arsenate. **267**

   If the incrustation contains organic substances of a humus-like nature, and further examination is required, the methods of organic chemistry should be used for the purpose (*cf.* Chap. III., No. 3). This examination cannot be carried out by the methods of analytical chemistry in the stricter sense, as dealt with in this book.

IV. ANALYSIS OF SOIL.

SEC. 191.

As in the case in the examination of water, quantitative analysis is really the only certain means of determining the value, *i.e.* the proportion of plant nutrients in soil, and, as in the case of drinking water, a definite conclusion is only possible when the geological and local conditions are taken into consideration, and the chemical analysis supplemented by bacteriological examination; in the same way a comprehensive opinion regarding a given soil can only be formed when the physical properties and the bacteriological results as well as the chemical composition are taken into consideration. For the analysis of soil, as was mentioned in connection with the analysis of water, reference should be made to R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, where indications, at all events, are given, even in regard to the physical and bacteriological examination.

The qualitative analysis of soil would almost seem to be superfluous, since, generally speaking, it would give the same results in all cases, at least as regards those earths on which plants can grow at all. Still, in qualitative analysis the extent of the reactions which occur permits of an estimation of the quantities of the constituents present, and consequently of a certain judgment as to the composition of the soil in question.

It should, however, be noted that for the nourishment of plants it is not only necessary for the respective constituents to be present at all, but for them to be present in a form in which they can be absorbed by the plants.

Thus, for example, potassium or also calcium will not serve for the nourishment of plants when it is present in the form of unweathered silicates which are not attacked by water containing carbon dioxide or humic acids.

It is important, therefore, in the analysis of soils to distinguish between the inorganic substances soluble in water, those soluble in acids, and those insoluble therein.

It should be borne in mind, when considering the different solubility of the substances present, that the various soils possess, to a greater or less degree, the capacity of fixing the constituents from aqueous solutions by means of adsorption, and then of again rejecting water (penetrating rain water) which does not contain these substances, or only to a slight extent. It is, therefore, as a rule, impossible to extract completely from the earth (even by frequently repeated extraction with water) the substances which are soluble in water. Despite these limitations, however, it is advisable to carry out the qualitative analysis in accordance with the solubility groups already mentioned. This examination may be divided as follows :—

1. Preparation and Examination of the Aqueous Extract.

SEC. 192.

268. A kilogramme of air-dried soil is used for the purpose. It is not easy to prepare a clear aqueous extract, since, when the soil is treated in the cold, or boiled with water in the ordinary way, and then filtered, the fine clay renders this work more difficult, in that it firstly stops up the pores of the filter paper, and secondly that it nearly always (at least at first) renders the filtrate turbid. The following process, devised by Fr. Schluze, is a simple and comparatively rapid method of attaining the object in view. The points of medium-sized funnels are closed with small filters made of strong paper; these are moistened and pressed well against the sides of the funnel, a layer of fine, pure, ignited quartz sand 2 to 3 cm. thick placed on them, and the air-dried earth, which is not powdered or only compressed (it is preferable that the greater portion should consist of lumps the size of a pea to that of a walnut), placed in the funnel so as to fill it to the extent of about two-thirds. Distilled water is now added until it covers the soil, the first filtrate, if turbid, being poured into the funnel again and allowed to drip through ; the funnel is again filled with water, and this process repeated until the filtrate is two to three times the weight of the soil used. The filtrates, which are often somewhat turbid, are mixed together ; a portion of the soil which has been extracted with water as far as possible is reserved.

The aqueous solution is divided into two portions, 1 and 2, containing two-thirds and one-third respectively.

1. Portion 1 is evaporated in a porcelain dish until very concentrated, and then tested as follows :—
    - **269** (*a*) A small quantity is filtered, the reaction of the clear or almost clear filtrate determined, one part of it reserved to be tested for organic substances according to (279), the remainder of the filtered portion heated, and treated with nitric acid. Evolution of gas indicates an *alkali carbonate.* One half of the liquid is then tested for *chlorine ion* by means of silver nitrate, and the other for *sulphate ion* by means of barium chloride.
    - **270.** (*b*) The remainder of the concentrated liquid obtained in 1, together with the precipitate which is usually formed, is placed in a small porcelain or, better, platinum dish, evaporated to dryness, and the brownish residue cautiously heated over a flame until the organic substances are destroyed. In the presence of nitrate ion incandescence will occur, which is more or less pronounced according to the quantity of nitrate ion. The gently ignited residue is tested as follows :—
        - (*α*) A small quantity is tested for *manganous ion* by fusion with sodium carbonate in the oxidation flame (Sec. 58, 19).
        - (*β*) The remainder is heated with water, a little hydrochloric acid added (effervescence indicates *carbonate ion*), the mixture evaporated to dryness to separate the silicon dioxide, the residue moistened with hydrochloric acid, water added, and the liquid heated and filtered.
            - (*aa*) The washed residue generally contains a little carbon, also some clay (if the aqueous extract was not quite clear), and finally *silicon dioxide.* To identify the latter, the point of the filter is pierced,

the residue washed through, boiled with a solution of sodium carbonate, the liquid filtered, treated with hydrochloric acid in excess, evaporated to dryness, and the residue treated with hydrochloric acid and water, whereby silicon dioxide is left.

(*bb*) A small portion of the hydrochloric acid solution is tested for *phosphate ion* (after previous evaporation following the addition of nitric acid) by means of a solution of ammonium molybdate in nitric acid ; a second portion is tested for ferric ion by means of potassium thiocyanate. To the remainder there are added (for the separation of phosphate ion) a few drops of ferric chloride, then, cautiously, ammonia solution until the liquid is slightly alkaline, the mixture gently heated, filtered, and the *calcium ion* precipitated from the filtrate by means of ammonium oxalate ; tests for the detection of *magnesium ion*, *sodium ion*, and *potassium ion* are made exactly as in the ordinary course of analysis (Secs. 172 and 173). Finally, a small portion of the pure alkali chlorides is spectroscopically examined for *lithium ion*.

271. Aluminium ion is not often present in the aqueous extracts of soils[1] (Fr. Schulze never found any). If tests are to be made for it, the precipitate obtained with ammonia is boiled with *pure* potassium or sodium hydroxide solution in a platinum or silver dish, the liquid diluted, and filtered, and the filtrate tested by acidifying it with hydrochloric acid, and heating it with ammonia. A positive result is only conclusive of the presence of aluminium ion, if the reagents were undoubtedly free from aluminium.

272. 2. One portion of the second part of the aqueous extract is tested, if iron ions were found, with potassium ferricyanide, and another portion with potassium thiocyanate, in both cases after the addition of a little hydrochloric acid, to determine the degree of valency in which the iron ions are present. The remainder of the aqueous extract is tested for *nitrate* and *nitrite ions*, and also for *ammonium* ion as in Secs. 236 and 237.

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[1] Soils which contain free sulphuric acid produced by the weathering of sulphur pyrites, and therefore yield aqueous extracts which show an acid reaction towards methyl orange, can, of course, contain aluminium ion *soluble in water*.

2. Preparation and Examination of the Acid Extract.

SEC. 193.

About 50 grms. of the soil which has been extracted as far as **273** possible with water (complete washing is, as a rule, not possible) is heated with moderately strong hydrochloric acid (effervescence indicates *carbonates*) for a few hours on the water bath, and filtered. The liquid, which is generally of a reddish-yellow colour, owing to ferric ion, is used for the following tests :

1. A small portion is tested for *ferric ion* by means of potassium thiocyanate, and a second for *ferrous ion* by means of potassium ferricyanide.
2. A small quantity is evaporated to dryness, the residue heated at **274.** a temperature only slightly exceeding 100°, moistened with hydrochloric acid, a little water added, the mixture heated, a little more water added, and the *silicon dioxide*, which is generally coloured, owing to organic substances, but turns white on ignition in the air, filtered off. A portion of the filtrate is tested with barium chloride for *sulphate ion*, and the remainder evaporated to a small residue, with the repeated addition of nitric acid, and this residue tested for *phosphate ion* by means of a solution of ammonium molybdate in nitric acid.
3. A somewhat larger portion is used for the detection of *manganous*, **275.** *aluminium, calcium, magnesium, potassium*, and *sodium ions* by the ordinary methods, and, if only small amounts of organic substances have passed into the hydrochloric acid solution, it is dealt with directly according to (111 *et seq.*), otherwise as in (135).
4. If it is desired to ascertain whether the hydrochloric acid extract **276.** contains *arsenic ion*, *cupric ion*, etc., the remainder of the solution is treated with hydrogen sulphide, etc., as described in (261) to (263).
5. If *fluorine ion* is to be detected, it is best to test a special portion of the ignited soil according to (230).

3. Examination of the Inorganic Constituents insoluble in Water and Acids.

SEC. 194.

277. When heated with hydrochloric acid (273), the greater portion of the soil always remains undissolved. If this is to be chemically examined, it should be washed, dried, the stones separated from clay and sand by sifting, these last separated by elutriation, and the different constituents submitted to the process of analysis described in connection with silicates (Sec. 181).

4. Examination of the Organic Constituents of Soil.

SEC. 195.

278. The organic constituents of soil consist partly of portions of plants, the structure of which can still be recognised (pieces of straw, roots, seeds of weeds, etc.), and partly of products of decomposition (especially those of plants), which are generally given the collective name of humus. These are of varying nature, according to their constituents and properties, and according to whether they are produced by the decomposition of substances containing or free from nitrogen—whether they have been produced with the assistance of alkalis or alkaline earths—and whether decomposition has just set in or is considerably advanced. These different constituents have not been exhaustively investigated. So far as they are known and characterised, they can only be in any way accurately identified by the methods of organic chemistry (Chap. III., No. 3). It generally suffices to estimate the quantity of carbon or nitrogen in them by means of elementary quantitative analysis, or to determine the quantity of permanganate necessary for their oxidation. In this respect reference should be made to R. Fresenius, *Anleitung zur quantitativen chemischen Analyse.* As far as qualitative analysis is concerned, which is the question here, the following tests should be made :—

(a) Examination of organic substances soluble in water.

279. The portion reserved for this purpose in (269) is evaporated to complete dryness on the water bath, and the residue treated with water.

The liquid is then filtered, and evaporated to dryness, and the residue ignited in the air. Incandescence, accompanied by an odour of burning, or previous carbonisation, indicates the presence of organic substances. If large quantities of humic substances soluble in water are present, the aqueous solution shows a more or less pronounced brown coloration.

(b) *Treatment with alkali carbonate.*

A portion of the soil which has been extracted with water is dried; **280** any stones or particles of straw, roots, etc., are separated from the finer soil by sifting, the latter treated for some hours at 80° to 90° with a solution of sodium carbonate, and the liquid filtered. The filtrate is treated with hydrochloric acid until the reaction is acid. If brown flakes separate, they are derived from the so-called humic acids, which were present in the soil in the form of salts insoluble in water. The precipitate is light or dark brown, according to the nature of the humic acid present.

(c) *Treatment with alkali hydroxide.*

The earth which was extracted in (*b*) with a solution of sodium **281.** carbonate is washed with water, and boiled for some hours with potassium hydroxide solution, the evaporating water being replaced; the liquid is then diluted and filtered, and the residue washed. The brown liquid is treated as in (*b*). The humic acids which separate here should be regarded as having been formed only on boiling with alkali hydroxide.

V. DETECTION OF INORGANIC SUBSTANCES IN THE PRESENCE OF ORGANIC SUBSTANCES.

SEC. 196.

In many cases the presence of organic substances renders the **282.** detection of inorganic substances simultaneously present much more difficult, whether it is a question of objects made of wood, leather, paper, or textile fabrics, etc., or of drugs, food products, spices, fodder, manure, lubricating oil, parts of plants, cadaveric remains, etc.

On the one hand, it is often impossible, without treatment, to dissolve the inorganic substances when solid matter or oils which do not mix with water and acids are to be examined. On the other hand, dough-like slimy masses often cannot be filtered without previous treatment, and, as in the case of many dark-coloured liquids, frequently make it impossible to recognise whether reagents produce precipitates, and if so, to determine their properties. Finally, even in clear solutions the reactions of many inorganic substances are influenced by the presence of organic substances (owing to the formation of complex compounds).

In many cases, therefore, the organic substances must be removed or destroyed.

According to whether the object in question is to be examined for all inorganic substances, or only for definite individual substances, various methods may be used. No one rule can be given to meet all cases. We therefore confine ourselves to giving a number of general instructions, and enlarging on a series of individual cases.

1. General Remarks.

283. 1. If it is solely a question of the examination of substances which do not volatilise on heating, solid substances may be calcined without treatment, but pasty or liquid substances only after evaporation to dryness. The method of procedure is described in detail in Sec. 208. If the object which is to be tested is not an unaltered part of a plant or of an animal body—if it is, for example, coloured, painted, impregnated, tanned, etc.—it may, of course, contain other substances than those dealt with in Sec. 208. In that case, the ash should be dealt with according to the methods given for the general systematic course of analysis. In the case of substances which burn with difficulty, complete incineration may, under certain conditions, be effected, if they are first impregnated with a solution of ammonium nitrate, or if the substance or the charcoal obtained by direct incineration is mixed with solid ammonium nitrate and heated. As a violent action may occur, the ammonium nitrate should be added cautiously.

In many cases it is preferable, instead of simply calcining the substance, to fuse it with sodium carbonate alone, or with sodium carbonate and potassium nitrate, which may be done according to the instructions given in Sec. 169 (135). It is not advisable to use sodium peroxide, owing to its violent action.

Needless to say, in the calcining or fusion process the individual constituents are not found in the same state of valency in the ash. It should also be noted that, for example, sulphur and phosphorus which were originally present in organic combination appear in the ash or fused mass as sulphate or phosphate ion, and cannot be distinguished from the sulphur or phosphorus originally present as a constituent of inorganic substances.

If a test is to be made for sulphate or phosphate ion in the presence of organic substances, the former should be dissolved in the manner described in 5 without destroying the organic substance, *e.g.* by extraction with acids. If it is only a question of the detection of chlorine, bromine, or iodine in organic substances, the latter should be mixed with about four times their quantity of pure sodium carbonate (if necessary evaporated to dryness), and gently ignited for some time. The carbonised mass is then extracted with water, and the liquid filtered from the charcoal, and tested for halogens.

2. Another method of destroying organic substances which may **284** be specially recommended in the case of liquid and semi-liquid objects, animal organs, cadaveric remains, and numerous viscous, slimy, or gelatinous masses which cannot be readily evaporated to dryness, is to heat them with strong oxidising agents. Mention may here be made of the method of primary importance proposed by R. Fresenius and von Babo, which depends on the action of hydrochloric acid and potassium chlorate. It is described in detail in Sec. 203 (rubric number 301). For particulars, therefore, reference should be made to the directions given there Instead of this method, the treatment with bromine of the articles in question on the water bath has also been suggested.

These excellent methods, which experience has shown to be trustworthy, cause decolorisation and the conversion of a pasty mass into a thin liquid, so that further treatment is possible; they do not, however, effect the complete removal of organic substances, and consequently these must be taken into consideration in the course of further examination, as being possibly present. Further, precipitates may be produced in such liquids by hydrogen sulphide or ammonium sulphide, even in the absence of the cations of Groups VI., V., and IV.

Other methods are based on as complete a destruction of the organic substances as possible. So far as the action of *concentrated* acids on organic substances is concerned, these can only be applied (after previous treatment of the liquids or pasty masses by the methods described in 2) to the precipitates obtained from such liquids, or to the residues which remained insoluble in the preliminary treatment. If solid substances are present, they may be directly oxidised by these methods.

The following reagents have been recommended: Red fuming nitric acid, concentrated sulphuric acid and nitric acid, ammonium persulphate and nitric acid, percarbonates, Caro's monosulphoperacid, H_2SO_5 (or concentrated sulphuric acid and 30 per cent. hydrogen peroxide (perhydrol), or ammonium persulphate [1]). These methods, if adopted, should be applied as described in detail in Sec. 197, *d* (292) and Sec. 205 (321).

285. 3. The destruction of organic substances by means of concentrated sulphuric acid is also suitable for many purposes, *e.g.* in the form in which it is described in the systematic course in Sec. 169 (135, *β*), or in the form which Kjeldahl has devised for the determination of nitrogen in organic substances, *i.e.* by heating them with a considerable excess of concentrated sulphuric acid, if necessary with the addition of phosphorus pentoxide or potassium sulphate, or mercury or cupric sulphate, until a light (usually clear) solution is obtained (*Zeitsch. anal. Chem.*, **40**, 566).

286. 4. If it is a question of solid substances, these may also first be extracted with water or acid, and only the residue subjected to one of the treatments described in 1–3. The same is applicable to masses from which the fluid portion may be readily separated by filtration.

287. 5. Under certain conditions, organic substances may be removed without destruction, *e.g.* when the object is mixed with oil or fat by treatment with ether or petroleum spirit, or the substances to be examined can be extracted from the organic material by means of a solvent which does not attack them. For instance, H. Fresenius and Schattenfroh (*Zeitsch. anal. Chem.*, **34**, 381) suggest shaking oils, which are to be tested for metals, with dilute acids, and so dissolving the metals.

Needless to say, in using the methods just described, it must in each case be borne in mind what constituents may possibly be lost by evaporation, what substances are introduced by the reagents into the object under examination, or may be formed in the treatment (thus, *e.g.* ammonia from organic nitrogen compounds on treatment as in 3), and the suitable method of treatment should be chosen accordingly.

288. 6. If salts or acids are to be detected in the presence of colloidal organic substances, it is frequently very advantageous to make use of dialysis (Sec. 9).[2] According to the conditions, the substance is introduced into the dialyser either at once or after previous treatment, *e.g.* after heating with hydrochloric acid, or with hydrochloric acid and potassium chlorate. If the former method is adopted, the substances will be present in the dialysate in the same stage of valency in which they were originally present. With regard to the procedure in detail, see Sec. 201.

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[1] *Cf.* for example, *Zeitsch. anal. Chem.*, **4**, 268; **21**, 306; **39**, 403; **42**, 544; **43**, 134; **44**, 259; **49**, 256; **50**, 307; **50**, 468; **51**, 78.

[2] *Cf.* O. Reveil, *Zeitsch. anal. Chem.*, **4**, 266; Bizio, *Ibid.*, **5** 51; Riederer, *Ibid.*, **7**, 517; H. Struve, *Ibid.*, **24**, 72.

It is, of course, impossible within the scope of this book to describe all the various methods which have been devised for the detection of particular substances in drugs, foods, articles of every-day use, urine, etc. In this respect reference must be made to the literature on the subject, especially to the *Zeitschrift für analytische Chemie*. In the following sections we only deal with a series of specially important cases of tests for poisonous constituents in the presence of organic substances, and also with the general method of examining plant ash.

2. Detection of Arsenic in Textile Fabrics, Carpets, Pigments, etc.

SEC. 197.

Of the many methods suggested for this purpose the following **289**
may be mentioned:—

(*a*) About 20 to 30 grms.[1] of the substance under examination (if necessary cut into small pieces) are covered in a retort (with a tubulure) of about 500 c.c. capacity, with 100 c.c. of pure hydrochloric acid of sp. gr. 1·19; the neck of the retort is drawn out and bent at an obtuse angle. It is placed in such a position that the part of the neck next to the body is directed diagonally upwards, and the other part is inclined downwards. The latter is introduced into the cooling tube of a Liebig condenser, and the joint secured with a piece of rubber tubing. The condenser tube is then conducted into a receiver of 700 c.c. capacity with a side tubulure, the connection being air-tight. This vessel is charged with about 200 c.c. of water, immersed in a basin of cold water to cool it, and its tube connected with a Peligot tube containing water. After about an hour, 5 c.c. of a cold saturated solution of ferrous chloride [2] prepared from crystals is introduced into the retort, and the contents heated. As soon as the excess of hydrochloric acid has escaped, the temperature is raised, so that the liquid boils; it is then distilled until the contents of the flask begin to froth up. It is allowed to cool, 50 c.c. of hydrochloric acid of sp. gr. 1·19 introduced into the retort, or into any other known arsenic distillation apparatus, and the liquid distilled in the same way.

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[1] If it is not possible or desirable to use so much of the substance, *e.g.* in the examination of dyes, the quantities of hydrochloric acid, ferrous chloride, etc., must be reduced in proportion to the amount of the substance; smaller retorts and apparatus should also be used.

[2] Instead of ferrous chloride, one of the other reducing agents mentioned in connection with pentavalent arsenic, Sec. 90, may be used.

The distillate, coloured brown by the organic substances, is combined with the contents of the Peligot tube, and diluted with water to about 600 or 700 c.c., and pure hydrogen sulphide introduced, first while the liquid is heated, and then in the cold.

After about 12 hours, the brown precipitate, consisting partly or wholly of organic substances, is collected on an asbestos filter (prepared by suitably packing asbestos into a funnel with a glass tap), the precipitate slightly washed, the tap closed, and the precipitate treated in the funnel with a few c.c. of a solution of bromine in hydrochloric acid of sp. gr. 1·19, the funnel being covered with a clock-glass. After about half an hour, the solution is run off into the precipitation flask, to the sides of which portions of the hydrogen sulphide precipitate are frequently still adhering. The residue on the asbestos filter is washed with the strong hydrochloric acid, already frequently mentioned, ferrous chloride in sufficient excess added to the contents of the flask, which are then rinsed with the aid of strong hydrochloric acid into a correspondingly smaller retort of a distillation apparatus, similar to the one mentioned above; the liquid is distilled to a fairly small residue, allowed to cool, and, after the introduction of another 50 c.c. of hydrochloric acid of sp. gr. 1·19 into the retort, distilled again. The distillate, which was mixed with the contents of the Peligot tube, is diluted to 500 to 700 c.c., and treated, as described above, with hydrogen sulphide, in order to separate any arsenic present as arsenious sulphide (R. Fresenius and E. Hintz). If it is desired to separate the arsenic as a mirror, the arsenious sulphide should be treated as in (311).[1]

290. (*b*) The following methods[2] used in Sweden are based on the same principle:—

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[1] The presence of arsenic in the substances under examination can only be considered to have been proved with absolute certainty when blank tests, made with the same hydrochloric acid and the same ferrous chloride in the same retorts, have given negative results. Atterberg (*Chem. Zentr.*, 1885, 600) prefers to evaporate the distillate containing arsenic with nitric acid, to dissolve the residue in water, and to convert the arsenate ion into silver arsenate.

[2] *Cf. Zeitsch. anal. Chem.*, **34**, 89.

A flask of about 300 c.c. capacity is connected by means of a 50 c.c. pipette, bent twice at right angles, with an open receiver. The latter has a capacity of about 100 c.c., and is half filled with water, in which the point of the pipette is slightly immersed; the sample is introduced into the flask, treated with 2 grms. of ferrous sulphate free from arsenic, and covered with 50–80 c.c. of concentrated hydrochloric acid of sp. gr 1·18–1·19, free from arsenic. In the case of bronze colours or other metallic substances, a further two to three grms. of ferric chloride free from arsenic should be added. The flask is heated, and the hydrochloric acid kept boiling as long as the pipette can be held in the hand. The resulting distillate is treated with 50 c.c. of saturated hydrogen sulphide water, or is diluted with 50 c.c. of water, and hydrogen sulphide introduced. After 12 hours' standing, the separated arsenic sulphide is collected on a small filter, washed with water until the acid reaction disappears, and then dissolved in 5 c.c. of dilute ammonia solution (one volume of ammonia of sp. gr 0·96 and one volume of water). After the addition of 0·02 grm of sodium carbonate, the solution is evaporated to dryness on a clock-glass, the residue thoroughly mixed with about 0·3 grm. of a mixture of dry sodium carbonate and potassium cyanide, and reduced in a current of carbon dioxide, as described in Sec. 89, 17, in a bulb tube made of glass absolutely free from arsenic. This tube must have a bulb of about 2 cm diameter, to which the narrow part of the tube in which the arsenic mirror is to separate is directly attached.

291 (c) The pigment, if present as such, is mixed with two parts of sodium carbonate and two parts of sodium nitrate, or the textile fabric or carpet, cut into small pieces, is saturated with a concentrated solution of this mixture, and thoroughly dried. Sodium nitrate is then fused in a small porcelain dish, and the substance, prepared in accordance with the instructions given above, gradually added to it, the heating being continued meanwhile, and, if necessary, a little more sodium nitrate being added from time to time. By this means a fused mass is obtained free from organic substances and carbon. When cool, it is soaked in water, the alkaline liquid filtered, the residue washed, sufficient hydrochloric acid added to the combined filtrate and washing water to expel the carbonic acid, nitrous acid, and nitric acid; the whole is then evaporated (at first on the water bath, finally at a slightly higher temperature) until heavy sulphuric acid vapour begins to escape, allowed to cool, diluted and filtered. This liquid may either be introduced directly into Marsh's apparatus to be tested for arsenic (Sec. 89, 12, 10), or it may be treated with hydrogen sulphide, after the addition of a few drops of hydrochloric acid, and any precipitate treated according to (311).

292. (*d*) Not infrequently, however, a simpler process will suffice to obtain a liquid from textile fabrics, carpets, etc., which can be tested directly in Marsh's apparatus. Of the many methods described for this purpose, mention may be made [1] of that recommended by H. Fleck.[2] The object to be examined, after being cut up, is digested for 18 to 24 hours with 50 to 100 grms. of pure 25 per cent. sulphuric acid at 50° to 60°. If, after this digestion, remains of the pigment are still visible on the object, which is very seldom the case, 3 to 5 grms. of pure nitric acid of sp. gr. 1·24 are added to each 100 grms. of the 25 per cent. sulphuric acid, and the digestion continued until every vestige of pigment has been destroyed. The liquid is filtered, the residue washed, and the filtrate diluted to 200 c c. and tested in Marsh's apparatus, 20 c.c. being introduced into it at a time. If nitric acid was added, the liquid must be evaporated until all the nitric acid has been removed before diluting it to 200 c.c.[3]

(*e*) Arsenic may, of course, be detected in a solution prepared according to (*d*) by one of the rapid methods described in Sec. 92, 9, (*e*) or (*f*), instead of with the aid of Marsh's apparatus.

(*f*) With regard to the official method of detecting arsenic and tin in coloured foods and spices, see *Zeitsch. anal Chem.*, **27**, 471.

3. Detection of Inorganic Poisons in Food, Cadaveric Remains, etc., in Chemico-legal Cases.[4]

SEC. 198.

293. The chemist is occasionally called upon to examine food, the contents of a stomach, a dead body, etc., for any poison contained in it, in order to determine whether the poisoning was voluntary or involuntary. Frequently, however, the question is more specific, and he is only required to decide whether a metallic poison is present in this or that substance, or, in particular, whether it contains arsenic, prussic acid, or another definitely specified poison, either because, on opening a body, the effects of poisoning or indications of a poison justify such a specific question, or that the coroner is in a position (or considers he is) to ask the question for other reasons.

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[1] In this connection, see also Sec. 211.

[2] *Zeitsch. anal Chem*, **22**, 474.

[3] With regard to other methods suggested for the same purpose, *cf.* H. Hager, *Zeitsch. anal. Chem.*, **11**, 478; E. Lyttkens, *Ibid.*, **22**, 147; G. Thomas, *Ibid.*, **22**, 475; Ed. Polenske, *Pharm. Zentralh.*, **40**, 388 (1889).

[4] *Cf.* R. Fresenius, *Über die Stellung des Chemikers bei gerichtlich-chemischen Untersuchungen, usw.*, *Liebig's Ann. d. Chem.*, **49**, 275; also R. Fresenius and L. v. Babo, *Über ein neues, unter allen Umstanden sicheres Verfahren zur Ausmittlung und quantitativen Bestimmung des Arsens bei Vergiftungsfällen*, *Liebig's Ann. d. Chem.*, **49**, 287.

Obviously the task is the easier to solve, the more specific is the question. But even when it only refers to a definite substance, *e.g.* arsenic, the chemist is wiser if he adopts a method which permits not only of the detection of one poison, possibly presumed to be present without valid reason, but also indicates the presence or absence of other similar poisons, for it must always be remembered that the object of his examination ("*corpus delicti*") is only available once.

If, however, this plan were to be carried to extremes, and a method devised to cover all possible poisons, it could obviously be worked out at a desk; practice, however, would prove only too soon that the inevitable complication of such a process would influence its easy application and the possibility of success to such an extent that the disadvantages would be greater than the advantages. Besides, as a rule, the accompanying circumstances permit of a fairly safe conclusion as to the group to which the poison must have belonged. With this point in view, the following processes are given:—

1. A process which ensures with the greatest certainty the detection of the smallest quantity of *arsenic* likely to be the subject of forensic examinations, which permits of its gravimetric estimation, and renders the *detection of all other metallic poisons* possible (Sec. 199 to Sec. 204).

2. A process for the detection of *hydrocyanic acid*, which does not render the substance useless for the examination for *metallic poisons*, or for *alkaloids* (Sec. 206).

3. A process for the detection of *phosphorus*, which does not interfere with the examination for other poisons (Sec. 207).

Further, as Appendix to I. :—

4. A process solely for the detection of arsenic, which, as a rule, cannot be used in conjunction with tests for other poisons (Sec. 205).

This chapter does not, therefore, claim to be a complete treatise on all chemico-legal examinations; what is stated, however, has been tested, and shown to be trustworthy by our own practical experience. The directions given here will, in most cases, be sufficient, especially as details will be given in an appendix to the chapter dealing with alkaloids of the best methods for their detection in forensic cases. It will be found advisable to instruct students in this toxicological work only when they have acquired thorough practice and experience in quantitative analysis.

294. If there are no definite indications of the nature of the poison to which the examination is to extend, so that it is necessary to take all poisons—inorganic as well as organic—into consideration, the material should be most cautiously examined with the naked eye or with a lens, and its odour, reaction, etc., tested; then, if circumstances do not permit of separate samples being taken for various examinations, the material is first tested for hydrocyanic acid and phosphorus (both can generally be detected by *one* distillation), then for alkaloids, and finally for metallic poisons.

If various objects are to be examined—drugs, foods, beverages, vomit, the contents of a stomach, intestinal contents, urine, organs of the body (liver, spleen, etc.)—it should be made a rule to examine the individual objects separately. It is always necessary, after weighing and uniformly mixing, to reserve one-third of each of the materials for unforeseen possibilities, and, if necessary, for determining in what state of combination the elements under suspicion are present.

In the case of material which putrefies readily, the portions reserved should be protected from decomposition by packing them in ice. In certain cases, they may be preserved by covering them with pure alcohol, or with saturated sodium carbonate solution.

1. Method for the Detection of Arsenic, while taking other Metal Poisons into consideration.[1]

SEC. 199.

295. Of all the metallic poisons arsenic is the most dangerous, and the one most frequently used—especially when poisoning is intentional. Among the arsenic compounds, again, arsenic trioxide (white arsenic) occupies the first position, firstly because its lethal dose is very small, secondly because it has little, if any, taste, and thirdly it is fairly easy to obtain.

Since arsenic trioxide only dissolves slightly and very slowly in water (owing to the fact that it repels the liquid), the greater portion of the quantity swallowed will, in the case of acute poisoning, be found still in the undissolved condition in the contents of the stomach or intestine; further, since the smallest granule may be detected immediately by means of a very simple test, and since, finally, it is certain (although arsenic is found in other compounds, in ferruginous deposits, coloured materials, etc.) that arsenic in granules or in powdered form can never be present in foods in the human body or in the putrefied material in coffins,[1] unless it has been directly placed there, special care should be attached to tests for isolating the actual arsenic, and this is generally successful. When making these tests, elementary arsenic, which may also be used for poisoning, may be found if it is still present as such.

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[1] Arsenic is usually spoken of as a "metallic poison," although in the chemical sense it belongs to the metalloids (*cf.* p. 315).

A. *Method of detecting undissolved white arsenic or elementary arsenic.*

SEC. 200.

1. If food, vomit, or the like is to be examined, the whole is **296** weighed, as far as possible uniformly mixed, and a third reserved for unforeseen possibilities; the other two-thirds are stirred in a porcelain dish with distilled water, allowed to stand for a while, and the liquid, together with the lighter floating particles, poured into another porcelain dish. This process is repeated several times and, if it is possible, with the same liquid, which for this purpose is poured from one porcelain dish into another. Finally, it is again elutriated, preferably in a glass dish, with pure water, the liquid removed as far as practicable, and careful note taken whether small, white, hard granules, sandy to the touch and gritty when rubbed with a glass rod, are found (these indicate white arsenic); or black grains or spicules (which indicate elementary arsenic). If no particles are observed, the examination should be continued as in Sec. 201 or 202; if found, however, the suspicious granules, or a part of them, are carefully picked out with forceps if possible, or they are cleaned, if very small, by further elutriation on a clock-glass, dried, weighed, and then the behaviour of one or more determined when heated in

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[1] R. Fresenius (*Zeitsch. anal. Chem.*, **6**, 195) once had occasion to examine the completely decomposed remains of a child, buried for a long time, which were in a small coffin painted with ochre paint. The lid of the coffin had an opening due to decay, and the rotten wood was mixed with the remains of the body. A small quantity of arsenic was present in the contents of the coffin, but not more than the quantity in the ochre paint on one of the surfaces of the coffin similar to the one that had fallen in. The human remains as such, therefore, contained no arsenic.

a small glass tube. In this test white arsenic yields a sublimate consisting of small lustrous octahedra and tetrahedra, but elementary arsenic at once gives an arsenic mirror. If the former is obtained, a further granule is tested for its behaviour when ignited with a splinter of charcoal (Sec. 89, 1). If this test yields an arsenic mirror, it affords a trustworthy proof that the granules under examination are arsenic trioxide. If it is a question of determining the weight of the arsenic, or if tests for other metallic poisons are to be made, the contents of both dishes are combined and dealt with according to Sec. 201 or 202.

2. If a stomach is under examination, its contents should be emptied into a porcelain dish, and the stomach turned inside out, and examined as follows: (*a*) The walls of the stomach for small, white, hard, sandy granules or for black granules or spicules. The parts to which they adhere are frequently red; the granules are often embedded in the skin. (*b*) After determining the weight of the uniformly mixed contents, two-thirds are treated as in 1; the remaining third is reserved.

Intestines are treated in exactly the same way as the stomach. If poisoning took place through the mouth, arsenic trioxide in granules or elementary arsenic cannot be present in other parts of the body, with the possible exception of the throat or the œsophagus.

If granules of this kind have been found, they are tested as in 1; otherwise, or if tests for other metallic poisons are to be made, the procedure given in Secs. 201 and 202 should be followed.

B. *Process for the detection of compounds of arsenic and other metals soluble in water or in hydrochloric acid by means of dialysis.*[1]

SEC. 201.

297. If, in testing according to A., no solid arsenic trioxide or arsenic was found, and the examination is, therefore, at once continued as in Sec. 202, by means of which the organic substances are entirely destroyed by potassium chlorate and hydrochloric acid, it is not necessary to examine the portion being tested for the state of combination in which the arsenic is present; a solution containing an arsenate ion is obtained, whether the arsenic was present in the elementary condition as trioxide, as arsenate, or as sulphide, etc. This difficulty can be at least partly overcome by introducing a test B. by means of dialysis between the two methods of treatment recommended in A. and C.

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[1] *Cf.* Sec. 9.

The apparatus shown in Fig. 7, p. 46, should be used for its application. The hoop consists of wood or preferably of gutta-percha, and is 6 cm. deep and about 20 to 30 cm. in diameter. When the dialyser has been perfectly arranged, the mass under examination (the residue and liquid from Sec. 200) is poured into it, after two-thirds of the cut-up stomach or intestine have been added, and the whole digested for 24 hours at about 32° ; the dialyser, charged with the liquid to at most a depth of 15 mm , is allowed to float on the water contained in the larger vessel, the quantity of which should be about four times as great as that of the liquid to be dialysed. After 24 hours half to three-quarters of the crystalloid substances will be found in the outer water, which generally appears colourless. It is concentrated by evaporation on the water bath, the greater portion finally acidified with hydrochloric acid, and treated with hydrogen sulphide, and the examination continued as in (302). If an arsenic compound, soluble in water (or another soluble metal salt) was present, the corresponding sulphide will be obtained in almost pure condition. In the end, all the soluble crystalloid substances may be extracted from the mass still contained in the dialyser, by allowing this latter to float repeatedly on further quantities of water. The residue of the dialysate, concentrated by evaporation, is finally tested as in Sec. 92, 13, to determine whether the arsenic found is present as arsenite or arsenate ion.

The contents of the dialyser, thus completely extracted with water, are, as a rule, best examined at once for metal compounds insoluble in water according to Sec. 203 ; in many cases, however, it may be advisable, especially in determining the stage of oxidation or the condition of combination of compounds of arsenic or other metals insoluble in water, first to heat the contents gently with dilute hydrochloric acid, and then to subject them again to treatment by dialysis.

If it is not desired to insert a test by dialysis between the two treatments of the material under examination according to Secs. 200 and 203 (the examination is naturally protracted), the remaining third of the material is used for the test by dialysis, in the event of a metallic poison having been found, for the purpose of determining more definitely the stage of oxidation and the form of combination of the metal, (*cf.* (319)), and this method of operation will in most be found to be preferable.

C. *Method of detecting arsenic, in whatever form of combination it is present, affording a means for its gravimetric estimation, and for determining the presence or absence of all other metallic poisons.*

SEC. 202.

298. If, in the process given in A., neither white arsenic nor elementary arsenic was found in solid form, and in the course of dialysis no arsenic compound soluble in water or dilute hydrochloric acid, it will be necessary to test the material for the purpose of determining whether arsenic is present in any other form. It was pointed out in Sec. 199 that *such* detection must not always be taken as an *indication of arsenic poisoning without further proof*. Let us admit the criticism based on Gautier's statement that arsenic in small quantity forms a *normal constituent* of the human body may be dismissed, since this statement of Gautier's has not been confirmed by the repeated experiments of other investigators, or at least has been recognised as being practically without significance.[1] On the other hand, however, it should be noted that traces of arsenic may certainly be found in the bodies of arsenic eaters, and especially that the urine of people who have been treated with salvarsan or other medicinal arsenic preparations may contain arsenic for weeks, and that arsenic is sometimes found in the hair and muscles of such persons, as well as being eliminated with their faeces.[2]

In the examination of exhumed bodies the fact should be borne in mind that the soil of *cemeteries* frequently contains appreciable quantities of arsenic The arsenic in soil cannot be dissolved by pure water, but it is converted into soluble compounds by mould fungi, as also by alkaline water, and especially by putrefying liquids. The force of the conclusions to be drawn from the detection of arsenic in an exhumed body is, therefore, considerably affected if, after destruction of the coffin, earth containing arsenic had come in direct contact with the decaying parts of the dead body (G. Popp[3]). According to H. Lührig tests should be made in such cases to see whether other bodies (not open to suspicion) from the same cemetery are, under the same conditions, free from arsenic.

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[1] Hödlmoser, *Zeitsch. physiol. Chem.*, **33**, 319 (1901). K. Czerny, *Ibid.*, **34**, 408 (1902). M. Dennstedt, *Ber.*, **44**, 10 (1911). J. Kratter, *Beiträge zur Lehre von den Vergiftungen*, 1905, p. 13. W. H. Bloemendal, *Arch. d. Pharm.*, **246**, 613 (1908).

[2] A. Valenti, *Chem. Zentr.*, 1912, I., 2049. Frenkel-Heiden and E. Navassart, *Ibid.*, 1913, III., 788.

[3] *Zeitsch Unters. Nahr. Genuss.*, **14**, 38. *Cf.* also F. Kratter, *Wiener klin Wochenschr.*, 1896, No 47.

Deductions from the results obtained from the examination of the remains of cremated bodies should be made with caution. In itself the detection of arsenic poisoning in such remains is quite possible, since, as was found by C. Mai and H. Hurt,[1] any arsenic administered remains as arsenate in the ash of the bones when calcined. In such cases, however, *large* pieces of bone, *still intact*, would have to be used for the detection of arsenic, and should be cleansed from foreign matter by scraping them with pieces of glass, since, in contrast to them, the *pulverulent portions* of the ash of the body may contain arsenic originating from the iron nails or screws of the coffin. Even the detection of arsenic in large pieces of bone cannot be considered proof of arsenic poisoning if the body was cremated in a zinc coffin, because the latter is also partly burned, so that zinc oxide containing arsenic may possibly come in contact with the bones, from which it cannot be removed or only with difficulty (see Mai[2]).

It is essential for the chemist to know *which portions* of the body submitted to him are of the most importance in the examination for arsenic. According to E. Ludwig,[3] arsenic may be much more easily detected in bones, in the case of both acute and chronic arsenic poisoning, although only absorbed by them in small quantity. It is found in larger quantity in the organs, especially in the liver, and next in the kidneys; the deposit of arsenic in the brain and muscles is considerably less. The *liver*—and possibly also the kidneys—are, therefore, the most suitable objects for examination for the forensic chemist, whilst the stomach and intestines are almost useless if death does not take place until several days after the poison has impregnated the body. In the case of *chronic* doses of arsenic (arsenic treatment), the arsenic accumulates to a large extent in the nails, hair, and skin. Arsenic is therefore not infrequently found in the hair, even when it cannot be detected in other organs; this is because many of our daily foods contain arsenic.[4]

If there is a suspicion that a post-mortem introduction of poison has taken place, it should be noted that, according to F. Strassmann and A. Kirstein,[5] in such cases, if the poison was introduced into the stomach, the arsenic is found in greater quantity in the *left* kidney, whilst the right kidney is free from arsenic, or has only absorbed traces thereof. In such cases, therefore, the chemist should make a separate examination of each kidney, the result of which is strengthened by a separate examination of the left and right lung, as also of the left and right sections of the liver. When there is reason to suppose that the poison has been introduced into the body elsewhere than the stomach, those organs in proximity to such parts and those at a distance from them should be examined separately.

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[1] *Zeitsch. angew. Chem.*, **17**, 1601.

[2] *Zeitsch. anal. Chem.*, **43**, 617.

[3] *Ibid.*, **20** 608.

[4] W. H. Bloemendal, *Arch. d. Pharm.*, **246**, 604 (1908).

[5] *Zeitsch. anal. Chem.*, **32**, 518; **36**, 347.

Needless to say, only vessels and reagents must be used for the examinations described below which have been proved by careful choice and testing to be free from arsenic compounds, and, in fact, free from heavy metal compounds and all impurities. The chemist who is constantly occupied with forensic poisoning tests would be well advised to devote a separate part of his laboratory solely to these examinations, and to furnish it with separate apparatus and reagents. The vessels in which the necessary tested reagents are kept should be labelled in different writing or in a different colour, *e.g.* red, from the stock vessels in the remainder of the laboratory.

The first process described is practically the one which R. Fresenius worked out so far back as 1844 in association with L. von Babo.[1] He used it frequently himself, and saw it used under his own supervision, and it always proved trustworthy. We also have had the same experience with it, and its accuracy and sensitiveness have been confirmed and admitted in other directions. In forensic cases it has the great advantage over Marsh's method, that it leaves the way clear for a test for all metallic poisons without other treatment, which is not the case with that method.

299. The process requires the following *reagents* and other chemicals, which can now be more readily obtained free from arsenic than was formerly the case, but for the preparation and purification of which the necessary instructions are nevertheless given here.

1. *Hydrochloric acid* of sp. gr. 1·10 to 1·12. To prepare it from the commercial hydrochloric acid containing arsenic, the latter, which should have a sp. gr. of at least 1·17, is treated with a concentrated solution of stannous chloride in the same hydrochloric acid, and in such quantity that after 24 hours a portion of the mixture, when treated with mercuric chloride solution, still gives a white precipitate, showing that stannous chloride is present in excess. The brown precipitate, containing all the arsenic and a little tin (Sec. 89, 15), is allowed to subside, the acid separated from the precipitate by decantation, and, if necessary, by filtration through

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[1] *Liebig's Ann. d. Chem.*, **49**, 308.

an asbestos filter, introduced into a retort, treated with a sufficient quantity (1 to 5 per cent.) of sodium chloride free from arsenic (if crude acid containing sulphuric acid was originally used), and distilled into a receiver without attachment containing 60 parts of water to every 100 parts of hydrochloric acid used, the distillation being continued until nearly all the acid has passed over. Or hydrochloric acid as concentrated as possible (of sp. gr. 1·17 to 1·19) is distilled with ferrous chloride. The first 30 per cent of the distillate collected contains arsenic, whilst the following 60 per cent. is free from arsenic, and has the required strength (H. Beckurts [1]). Finally, hydrochloric acid free from arsenic may be prepared by distilling sodium chloride with sulphuric acid, both of which have previously been completely freed from arsenic by the methods described below (Nos 5 to 10). The following methods are suitable for testing hydrochloric acid for traces of arsenic. (*a*) One litre of the acid is heated with a little *pure* ferrous chloride in a distillation apparatus, and the first 50 c.c. collected tested by means of arsenic-free zinc, to determine whether, when tested by the methods described in Sec. 92, 9, *e* and *f*, it is free from arsenic, also whether it leaves any trace of an arsenic deposit in the glass tube of the apparatus described in Sec. 89, 12, even when the test is continued for a long time. (*b*) One litre of the acid is evaporated to a small residue (after the addition of sufficient water to reduce the specific gravity to at most 1·104, and of *a few* granules of pure potassium chlorate) in a basin of pure porcelain, a little water being added from time to time, and the residue then tested in Marsh's apparatus as described in (*a*).[2]

The *ferrous chloride* for use in the test (*a*) is prepared by dissolving iron wire in hydrochloric acid of sp. gr. 1·10 to 1·12, the solution being continuously heated in a small distillation apparatus. When no more arsenic can be detected in the distillate, the remainder of the solution is free from arsenic.

2. *Potassium chlorate.* The commercial product is purified, if necessary, by repeated re-crystallisation, one part being dissolved each time in twice its quantity of boiling water, or treated in the manner described in No. 10. *To test it*, a fairly large quantity is finally re-dissolved in twice its weight of boiling water, and allowed to crystallise, being stirred from time to time. When completely cold, the crystals are separated by means of a Witt filter plate, the resulting mother liquor decomposed by heating it with dilute

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[1] *Zeitsch. anal. Chem.*, **24**, 483.

[2] R. Otto, *Anleitung zur Ausmittelung der Gifte*, 7th ed., p. 163 (1896).

hydrochloric acid free from arsenic, and lastly one portion tested for the ions of heavy metals in general, by treatment with hydrogen sulphide and ammonium sulphide, and another portion evaporated to a small residue, with the occasional addition of a little water, this residue left on the water bath until the odour of chlorine disappears, and its solution tested in Marsh's apparatus.

3. *Hydrogen sulphide.* The gas produced by the action of hydrochloric acid or sulphuric acid on iron sulphide often contains a little hydrogen arsenide, owing to the presence of arsenic in the original substance, and consequently, in forensic examinations, should not be used or at least only after being previously purified. For the latter purpose, a process devised by O. Jacobsen[1] is the most suitable; it depends on the conversion of hydrogen arsenide, by means of iodine at the ordinary temperature, into arsenious iodide:

$$AsH_3+3I_2=AsI_3+3HI$$

whilst hydrogen sulphide does not act upon solid iodine. The hydrogen sulphide is conducted through a U-tube about 17 cm high and 15 mm. wide, in which coarsely ground air-dried iodine is loosely packed in layers between glass wool. A calcium chloride cylinder is placed in front of the iodine tube and a washing flask with water behind it.[2] *The preparation of gas from substances free from arsenic*, including alkaline earth sulphides, is safer than purifying it. According to Kosmann's communication, Rivot used *barium chloride* 50 years ago; R. Otto[3] recommends calcium sulphide. He gives the following directions for its preparation and the evolution of gas from it, and we have found them satisfactory. Seven parts of calcined gypsum, three parts of powdered charcoal, and one part of rye meal are mixed to a stiff paste, and this made into balls or rolls, and completely dried and ignited at a bright red heat. The balls are placed in a Woulfe flask, one tubulure of which is fitted with a dropping funnel provided with a tap, whilst an outlet tube for the gas is attached to the other. If pure hydrochloric acid is allowed to drip from the funnel on to the calcium chloride (treated with water), a fairly steady current of pure hydrogen sulphide will be evolved, especially if the vessel is sufficiently shaken. In the particularly suitable method devised by R. Fresenius[1] four parts of the calcium sulphide, obtained as described above, are mixed with one part of calcined gypsum and the requisite quantity of water to a thick paste, this laid on square flat paper capsules, the hardened but still moist mass taken out, and the slabs, which are about 15 mm. thick, cut into cubes and dried at a gentle heat. These are then decomposed in a Kipp's apparatus with pure hydrochloric acid.[2] *To test* the hydrogen sulphide, it is introduced in sufficient quantity into hot pure nitric acid, the latter evaporated, subsequently with the addition of pure sulphuric acid, and the residue tested in Marsh's apparatus (Zd. Skraup).

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[1] *Zeitsch. anal. Chem.*, **29**, 737; *cf.* also O. Brunn, *Chem. Zentr.*, 1888, 1376; Zd. H. Skraup, *Zeitsch. anal. Chem.*, **37**, 322.

[2] Other methods of purification depend on the combination of hydrogen sulphide with magnesia to form magnesium hydrogen sulphide, from the solution of which a gas free from arsenic is obtained on heating (Divers and Shimidzu, *Zeitsch. anal. Chem.*, **24**, 243), or on passing the gas over potassium sulphide heated to 350° (O. v. d. Pfordten, *Ber.*, 17, 2897), or on washing the gas by means of a system of flasks containing hydrochloric acid of various concentrations (W. Lenz, *Zeitsch. anal. Chem.*, **22**, 393).

[3] *Anleitung zur Ausmittelung der Gifte*, 7th ed., p. 175 (1896).

4. *Red fuming nitric acid.* This may be prepared by distillation of sodium nitrate with sulphuric acid, both of which have previously been completely freed from arsenic by the method given below. For the purpose of the test, a fairly large portion is evaporated as completely as possible in a porcelain dish, on the water bath, with a few c.c. of sulphuric acid free from arsenic and the residue heated on a sand bath until sulphuric acid vapours begin to be evolved. When cold, it is taken up with water and the aqueous solution tested, on the one hand, with hydrogen sulphide and ammonium sulphide, and, on the other, in Marsh's apparatus.

5. *Concentrated sulphuric acid.* According to Lockemann,[3] purification is best based on the behaviour of hydrogen chloride with arsenious and arsenic acids, which may be expressed by the following formula: —

$$H_3AsO_3+3HCl \rightleftarrows AsCl_3+3H_2O$$
$$H_3AsO_4+5HCl \rightleftarrows AsCl_3+4H_2O+Cl_2$$

If the products of reaction shown on the right are allowed to volatilise, and fresh hydrogen chloride repeatedly added, all the arsenic must finally be expelled. Hydrogen chloride is then continually introduced into sulphuric acid heated to about 250° in a porcelain vessel, which is meanwhile rotated (mercury seal); the gas evolved gradually carries off all the arsenic, and is absorbed in water. The test is made, after dilution with water, in Marsh's apparatus, pure zinc being used.

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[1] *Zeitsch. anal. Chem.*, **26**, 339 (1887).

[2] With regard to other methods for obtaining hydrogen sulphide free from arsenic, *cf. Zeitsch. anal. Chem.*, **23**. 280; O. v. d. Pfordten, *Ber.*, **17**, 2898; W. Hampe, *Zeitsch. anal. Chem.*, **31**, 557; J. R. Michler, *Ibid.*, **37**, 322; **41**, 370.

[3] *Verhandl d. Ges. Deutsch, Naturf. Ärzte*, 79. Vers. zu Dresden, **1907**, II., **1**, 145.

6. *Zinc.* According to R. Otto,[1] pure zinc free from arsenic can, generally speaking, only be prepared from pure zinc oxide free from arsenic; it must, therefore, be bought and carefully tested. For this purpose the whole quantity is fused in *one* operation and granulated. If, on testing, part of the quantity is found to be pure, the whole may be considered pure. The absence of arsenic is determined by means of Marsh's apparatus, a not too small quantity (up to 50 grm) being *completely* dissolved in sulphuric acid free from arsenic. The zinc must not only be free from arsenic, but also *absolutely free from metal sulphides*, since otherwise in Marsh's test, a yellow mirror of arsenious sulphide may be formed instead of a dark arsenic mirror.

7. *Sodium carbonate.* An absolutely pure salt is best obtained from sodium hydrogen carbonate. The latter is first placed in a funnel loosely packed with cotton wool, or in a small porcelain dish covered with filter paper, treated several times with small quantities of cold water, dried, and finally converted into carbonate by heating it for half an hour at 270° to 300° on the sand bath, with continual stirring. It should dissolve in water to a clear solution; the solution, when heated with nitric acid and ammonium molybdate solutions, should neither turn yellow nor give a yellow precipitate; no precipitate should be formed by hydrogen sulphide in the solution acidified with hydrochloric acid, or by ammonium sulphide solution in the neutral solution. The solution of the salt, acidified with nitric acid free from arsenic, is tested in Marsh's apparatus.

8. *Potassium cyanide.* When continuously heated in a small porcelain boat in the apparatus described in Sec. 89, 17, a mixture of one part of the salt with three parts of sodium carbonate free from arsenic should not show any trace of a deposit in the glass tube.

9. *Sodium nitrate.* Purification is carried out on the lines described in 10. It should dissolve to a clear solution in water. When heated with a solution of ammonium molybdate in nitric acid, the solution should not give a yellow precipitate; no precipitate should be formed by hydrogen sulphide in the acidified solution, nor by ammonium sulphide solution in the neutral solution. A solution of the salt is evaporated on the water bath with an excess of sulphuric acid free from arsenic, fresh water being continually added, the residue is heated on a sand bath until the first appearance of the vapours of sulphuric acid, cooled, taken up with water, and tested in Marsh's apparatus.

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[1] *Anleitung zur Ausmittelung der Gifte*, 7th ed., p. 189 (1896).

10. ***Sodium chloride and other neutral salts**, e.g. **also potassium chlorate or sodium nitrate***, may, according to G. Lockemann,[1] be completely freed from arsenic by means of the properties of adsorption of ferric hydroxide. 900 mgrms. $Fe(OH)_3$ are sufficient at a temperature of 25° to remove 50 mgrms. of arsenic from almost saturated aqueous salt solutions, the reaction is somewhat weaker at a higher temperature. The respective neutral or slightly acid solution is treated with iron alum solution, just sufficient ammonia solution added in the cold to precipitate the hydroxide completely, and the liquid filtered after half an hour's standing. To test the salts obtained by crystallisation from the solutions thus treated, the procedure given in connection with sodium nitrate should be followed.

11. *Filter paper.* Filter papers washed with acids should be used (p. 39). They are tested by placing a number of them inside each other in a glass funnel, the tube of which is fitted with a tap. The tap is closed, the funnel filled with hydrochloric acid free from arsenic, and, after being covered, allowed to stand for half an hour. The tap is then opened, the acid allowed to drain off, the filter washed with a little water, and the filtrate tested as in 1.

12. *Glass tubes.* It is essential that the tubes used for the reduction test of R. Fresenius and von Babo (311), or for the production of Marsh's arsenic mirror (320), should be of glass free from arsenic, since otherwise—especially when in Fresenius and von Babo's test the fused mixture comes in contact with the glass when it froths up or spurts—deceptive mirrors, due to the arsenic contained in the glass, may be obtained. To test the tubes, a blank Fresenius and von Babo test (omitting the little boat) or Marsh test should be made, only reagents absolutely free from arsenic being used. At one time glass tubes free from arsenic were difficult to obtain,[2] but they can now be readily procured.

SEC. 203.

We now come to the actual method of procedure. The mass, **300.**
diluted during elutriation in the process A., is evaporated in a porcelain dish on the water bath until it is of a pasty consistency. (If it was acid, pure sodium carbonate should previously be added until it is slightly in excess.) To this residue is added (if it was not done

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[1] *Verhandl. d. Ges. Deutsch. Naturf. Ärzte*, 79, Vers. zu Dresden, 1907, II., **1**, 145; *cf.* also *Zeitsch. anal. Chem.*, **51, 717**.

[2] W. Fresenius, *Zeitsch. anal. Chem.*, **22**, 397 (1883). R. Otto, *Anleitung zur Ausmittelung der Gifte*, 7th ed., p. 211 (1896).

during dialysis) two-thirds of the cut-up stomach, intestine, etc. If other portions of a body are to be examined (lungs, liver, etc.) they should also be cut into small pieces, preferably with scissors, and two-thirds used for the test. As a rule—and apart from the special cases mentioned on p. 734—it is advisable not to mix the various organs, but to examine them separately, as only then can a conclusion be drawn from the quantity of arsenic found in the individual organs, and from the known average weight of the organs, as to the total quantity of arsenic present in the whole body, a point which is of the greatest importance for medical and legal experts.

Should for any reason the objects under examination contain alcohol, it must always be removed first by evaporation on the water bath.

The examination is divided into three sections :—

301. 1. *Decolorisation and solution.* Sufficient pure hydrochloric acid of sp. gr. 1·10 to 1·12 is added to the objects in a porcelain dish (the quantity of which may, as an example, be taken to be 100 to 250 grms.) until its weight is approximately the same as that of the dry substance in the mixture, and further, sufficient water to give the whole the consistency of a thick paste. The hydrochloric acid added should never be more than a third of the whole liquid present. At the outset about 2 grms. of potassium chlorate[1] are added, and the mixture heated on the water bath. When the liquid has reached the same temperature as the bath, further quantities of 0·5 to 2 grms. of potassium chlorate are added at intervals of 5 to 10 minutes, with constant stirring, until the contents of the dish have become fairly homogeneous mobile, and, as a rule, pale yellow, and retain this colour on further heating for 15 to 30 minutes. The evaporating water should be replaced from time to time. When this point has been reached, a little more potassium chlorate is added, and the dish removed from the water bath. When quite cold, the contents are carefully transferred (according to the quantity) to a linen strainer or a filter, the liquid allowed to drain off, and heated for a while on the water bath (the evaporating water being replaced) until the odour of chlorine has entirely, or almost entirely, disappeared. The residue, which we will call I., is thoroughly washed with hot water, dried, distinctly marked, and reserved for further examination as in (313). The washings are evaporated on the water bath to about 100 c.c., and this liquid, together with any precipitate formed in it, added to the main filtrate.

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[1] If no potassium ion is to be introduced into the mass, pure chloric acid is recommended instead of potassium chlorate by Sonnenschein and Jeserich as producing the best results, *cf. Zeitsch. anal. Chem.*, **22,** 472.

When *mercury* is present, it must, under certain conditions, be taken into account that a portion of it will not have been dissolved. At least, M. T. Lecco[1] reports that in a case of poisoning with metallic mercury the particles which remained in the stomach could easily be removed, since mercury is only dissolved with difficulty by hydrochloric acid and potassium chlorate. Further, E. Ludwig[2] points out that mercuric ion can form mercuric sulphide with the sulphur of proteins, and that this requires a considerable quantity of potassium chlorate to render it soluble. For these and other reasons, the yellow crumbly masses which are obtained on the destruction of organic substances by hydrochloric acid and potassium chlorate may, according to E. Ludwig,[3] obstinately retain mercury (up to 40 per cent. of that present). This difficulty may be overcome by decomposing the proteins of the object under examination by heating it for several hours with hydrochloric acid prior to the oxidation with potassium chlorate. This is not permissible, however, if a test for arsenic is to be made. In view of all these possibilities, portions of the mercury can remain in the residue I. (*cf.* (313)).

R. Fresenius found after repeated tests, in which the same strength of hydrochloric acid was used (1 part of acid of sp.gr. 1·12 and 2 parts of water), that the frequently expressed fear that in the methods described arsenic, antimony, or tin would *volatilise* was *without foundation.*

In the case of *urine*, treatment with hydrochloric acid and potassium chlorate is usually unnecessary. It may, as a rule, be subjected directly to the treatment with hydrogen sulphide described in (302), after acidification with hydrochloric acid.

Other methods for the destruction of organic substances have frequently been described. A summary of them has been given by B. J. Gadamer[4] (*cf.* also (284), (285), (321)).

2. *Treatment of the solution with hydrogen sulphide* (*separation as arsenic sulphide of the arsenic ion present, or separation of all metallic poisons of the fifth and sixth groups as sulphides*). 30

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[1] *Ber.*, **24**, 928 (1891).

[2] *Chem. Zentr.*, 1892, II., 941.

[3] *Zeitsch. anal. Chem.*, **30**, 654 (1891).

[4] *Lehrbuch. d. chemischen Toxikologie*, p. 141 (1909).

The liquid obtained in 1 (about four times the quantity of hydrochloric acid used) is placed in an Erlenmeyer flask, heated on the water bath at 70°, and a slow current of washed hydrogen sulphide passed through it for about 12 hours; the liquid is allowed to cool while the introduction of the gas is continued, the inlet tube for the gas rinsed with a little ammonia solution, the ammoniacal solution obtained added to the main liquid after acidification, and the flask containing them covered with filter paper and allowed to stand in a fairly warm place (30°) until the odour of hydrogen sulphide has almost disappeared. The resulting precipitate is collected on not too large a filter, and washed with hydrogen sulphide water until the washings no longer contain chlorine ion. The filtrate and the washings are evaporated after renewed saturation with hydrogen sulphide. If a precipitate separates, it is filtered off, washed, and added to the main precipitate produced by hydrogen sulphide. The filtrate, concentrated by evaporation, is treated in a flask of suitable size with ammonia solution until the reaction is alkaline, then with ammonium sulphide solution, and the almost full flask tightly corked, and allowed to stand for a while until required for testing as in (317).

03. 3. *Purification of the precipitate produced by hydrogen sulphide.* The precipitate obtained in 2, which, in addition to organic substances and free sulphur, must contain all the arsenic in the form of arsenious sulphide, as, in fact, all the metallic poisons of the fifth[1] and sixth groups as sulphides, is thoroughly dried, with the filter, in a small porcelain dish heated on the water bath; pure fuming nitric acid, in particular free from chlorine, is added, drop by drop, until the whole of the precipitate is moistened, the whole evaporated to dryness on the water bath, and, if necessary, this treatment with nitric acid repeated. Pure concentrated sulphuric acid, previously heated, is added to the residue until this is uniformly moistened, the mixture heated on the water bath for two or three hours, finally at a somewhat higher, though always moderate temperature (170°) in an air, sand, or oil bath, until the carbonised mass is of a friable consistency, and until a small sample (to be added to the whole later), mixed with water, yields, on settling, a colourless or almost colourless, but not a brown, liquid. Should this not occur, but the residue consist of a brown oily liquid, a piece of pure, well washed and dried filter paper is added, and the heating continued. The temperature may be safely raised until sulphuric acid vapour begins to escape; no loss of arsenic need be feared. If these rules are observed, the object in view, *i.e.* the destruction of organic substances without the loss of any metal, will have been satisfactorily attained. The residue is heated on the water bath for a short time with a small quantity of a mixture of 8 parts of water and 1 part of hydrochloric acid, the liquid filtered, the residue repeatedly washed with small amounts of hot distilled water to which a little hydrochloric acid is added, the washing completed with boiling water, and the last washings (if necessary concentrated by evaporation on the water bath) added to the filtrate and the first washings.

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[1] Lead sulphide and cadmium sulphide are not precipitated from *very acid* solutions. Should, for this reason, the lead or cadmium ion have remained in solution, it will be found in the precipitate produced by ammonium sulphide solution (317). With regard to mercury which was not precipitated, *cf.* (301) or (313).

The washed carbonised residue, which we will call II., is dried and put aside, distinctly marked, for further tests as in (314).

4. *Preliminary test for arsenic and other metallic poisons of the fifth and sixth groups (second precipitation with hydrogen sulphide).* **304.** A small portion of the clear or at most slightly yellow liquid obtained in (303), which contains all the arsenic as arsenate ion, and may also contain the ions of tin, antimony, mercury, copper, bismuth, and cadmium, is gradually and carefully saturated with a mixture of ammonium carbonate solution and a little ammonia solution, and note taken whether a precipitate is formed or not. When this point has been decided, the sample is acidified with hydrochloric acid, whereby any precipitate resulting from the ammonium carbonate re-dissolves, the sample returned to the main liquid, and this treated continuously with hydrogen sulphide exactly as described in (302), first with gentle heating and then without heat. Three different results may be obtained, which must be carefully distinguished.

(*a*) *For some time no precipitate is formed by hydrogen sulphide,* **305.** but on standing a slight precipitate of a white or yellowish-white colour is produced. In this case there are, in all probability, no ions of the fifth and sixth groups present. Nevertheless, the separated and washed precipitate is treated as in (308), in order that even the smallest traces arsenic, etc., may not be overlooked.

306. (*b*) *A pure yellow precipitate of the colour of arsenic sulphide is formed.* A small portion of the liquid is taken, together with the precipitate suspended in it, a little ammonium carbonate added, and the whole shaken for a while without being heated. If the precipitate dissolves readily and, excepting for a trace of sulphur, completely, and if no precipitate was formed with ammonium sulphide when testing a sample in (293), then arsenic but no other metallic poison is present (at least no appreciable quantity of any other, *i.e.* tin or antimony, is present). The solution of the small sample in ammonium carbonate is treated with hydrochloric acid until the reaction is acid, the sample thus acidified returned to the liquid containing the main precipitate, and the examination continued as in (308). If, on the other hand, the precipitate does not dissolve or only incompletely in ammonium carbonate solution, or if a precipitate is formed in the test with ammonium carbonate in (304), there is reason to assume that another metallic poison is present, possibly in addition to arsenic. Hydrochloric acid is also added to the sample in the small tube until the reaction is acid, the mixture returned to the liquid containing the main precipitate, and the examination continued as in (309)

307. (*c*) *A precipitate of another colour is formed.* It must be assumed that other metallic poisons are present, possibly in addition to arsenic. The examination is made as in (309).

308. 5. *Treatment of the pure hydrogen sulphide precipitate, if there is reason to assume in* (306) *that arsenic is present. Gravimetric estimation of the arsenic.* As soon as the liquid treated with hydrogen sulphide in (304) has almost lost its odour of the gas, the yellow precipitate is separated on a small filter which has been dried at 100° and weighed, washed first with water, then with absolute alcohol, and finally with pure benzene or petroleum spirit, in order to remove any sulphur mixed with the arsenious sulphide. When the benzene or petroleum spirit has been removed by the renewed use of absolute alcohol, the filter containing the precipitate (if the quantity of this is considerable) is dried at 100° until the weight is constant. If, on the other hand, the precipitate is very slight, it is freed from any sulphur, washed with water, and dissolved in ammonia solution, the filter (on which, in this case, nothing insoluble can have remained) is thoroughly washed with dilute ammonia solution, the ammoniacal liquid evaporated in a small, carefully-weighed porcelain crucible on the water bath, and the residue dried at 100° until it no longer loses weight, and then weighed. If, after reduction as in (311), it was evident that the former precipitate or this residue consisted of perfectly pure arsenious sulphide, each part of it corresponds to 0·8042 part of arsenic trioxide or 0·6092 part of arsenic. The treatment of the precipitate, or of the residue in the crucible, is then continued as in (311).

309 6. *Treatment of the pure hydrogen sulphide precipitate, if there is reason to assume in (306) or (307) that another metallic poison—possibly in addition to arsenic—is present. Separation of the metals from each other. Gravimetric estimation of the arsenic.*

If there is reason to assume that other metals are present—possibly in addition to arsenic—in the liquid treated in (304), the precipitate is filtered off (as soon as the precipitation with hydrogen sulphide is quite complete and the odour of the gas has almost disappeared) on to a small hardened filter, thoroughly washed, the point of the filter pierced, and the precipitate washed by means of a jet with as little water as possible into a small flask placed beneath it. The liquid in which it is suspended is treated first with ammonia solution and then with ammonium sulphide solution,[1] digested for a while at a gentle heat, then filtered from any insoluble precipitate which is left. The precipitate, which we will call III , is washed off the perforated filter with a jet of water and put on one side, carefully marked, for further examination as in (315). The solution or the filtrate is evaporated to dryness, together with the washings, in a small porcelain dish. The residue is treated with a little pure fuming nitric acid (free from chlorine), the acid almost completely evaporated, and, as was originally recommended by C. Meyer, a solution of pure sodium carbonate added in small quantities until it is in excess. Next a mixture of 1 part of sodium carbonate and 2 parts of sodium nitrate is added in sufficient but not excessive quantity, the whole evaporated to dryness, and the residue heated very gradually in a porcelain crucible until the mass, which at first becomes brown and then black, becomes colourless If cupric sulphide was dissolved by the ammonium sulphide solution, the fused mass remains grey to black.

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[1] If the precipitate contained *cupric sulphide*, a little of the latter is generally dissolved by the ammonium sulphide ; this is, of course, taken into consideration in (316). If copper is to be excluded in this case, a solution of *sodium hydrogen sulphide* (prepared from sodium hydroxide solution free from arsenic, and hydrogen sulphide also free from arsenic) is used instead of ammonium sulphide solution. If preferred, the sulphides (of arsenic, antimony, and tin) which have been dissolved are re-precipitated from the filtered solution by means of dilute hydrochloric acid, collected on a filter, washed with hydrogen sulphide water, and re-dissolved in ammonium sulphide solution (R. Otto).

310. When cool, the fused mass is extracted with cold water. If a residue remains, it is filtered off (we will call it IV.), washed with a mixture of equal parts of alcohol and water, and reserved for further examination as in (316). The solution, in which all the arsenic should be contained as arsenate ion,[1] is mixed with the washing liquid (concentrated by evaporation and freed from alcohol), the mixture gradually and carefully acidified with pure dilute sulphuric acid, evaporated in a small porcelain dish, the highly concentrated liquid tested by the further addition of sulphuric acid, to see whether the quantity of the latter was sufficient to expel all the nitric and nitrous acid, and finally carefully heated until heavy vapours of sulphuric acid begin to escape. To the cooled residue 5 to 10 c.c. of a solution of sulphur dioxide in water is added, in order to reduce the arsenate ion to arsenite ion, the mixture heated on the water bath until the excess of sulphur dioxide has escaped, diluted with a little water, the solution poured into a small narrow flask, and, while it is being heated at 70°, a slow current of washed hydrogen sulphide introduced for about six hours; finally it is allowed to cool, the introduction of the gas being continued meanwhile. If arsenite ion is present, a yellow precipitate is formed. This is filtered off as soon as it has completely subsided, and the liquid has almost lost its odour of hydrogen sulphide, washed as described in (308), and its weight determined by means of one of the methods also described there.

311. 7. *Reduction of the arsenious sulphide.* The greatest care must be taken in the preparation of elementary arsenic from arsenious sulphide, since it should be the final proof of the presence of arsenic. The best and most certain method to use is that recommended in Sec. 89, 17, *i.e.* to fuse the arsenic compound, mixed with potassium cyanide and sodium carbonate, in a small porcelain boat in a slow current of carbon dioxide. This process is especially suitable in forensic cases, since, apart from the advantage of greater accuracy, it offers a guarantee against any confusion of arsenic with another substance (especially antimony). Great care should be taken that the whole apparatus is filled with carbon dioxide, that the contents of the little boat are thoroughly dried, and do not spirt even when heated, and that the current of gas is of the right strength before heating. Direct heating of the mixture of potassium cyanide, sodium carbonate, and the substance to be examined for arsenic in a glass tube, without the use of the little boat, is only permissible when in another part of the same tube a fusion test with potassium cyanide and sodium carbonate in a slow current of carbon dioxide has yielded no trace of an arsenic deposit (*cf.* pp. 351 and 739). Apparatus for the evolution of carbon dioxide in which the current of carbon dioxide cannot be regulated must not be used for this important test.

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[1] If the substance under examination should contain a *thallium compound*, all the arsenic would not be present in this solution, since it would have been only incompletely dissolved on treatment of the orange-coloured solid solution of thallous sulphide in arsenious sulphide with ammonium sulphide (*cf.* (315)).

For the purpose of reduction, the arsenious sulphide obtained may be used directly. If it could be collected on a weighed filter, only a small portion is used, so that the reduction may, if necessary, be repeated. If, on the other hand, the precipitate of arsenious sulphide was so small that it had to be removed from the filter by means of ammonia solution, the residue obtained from the evaporation of the ammoniacal solution is re-dissolved in a little ammonia solution, 0·02 to 0·04 grm. of powdered anhydrous sodium carbonate [1] added, the whole evaporated to dryness on the water bath, with constant stirring, and small portions of this mass used for the reduction.[2]

When this operation has been completed the reduction tube **312.**
(Fig. 52) is cut off between the constricted part and the place where the boat stood; the front part (containing the arsenic mirror) is put aside, whilst the boat is covered with water, the solution filtered when the saline mass has separated, and the latter treated with hydrochloric acid until it is acid; hydrogen sulphide is now introduced, and a note taken if a precipitate is formed. If the arsenious sulphide has been reduced as such,

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[1] Blomqvist prefers sodium hydrogen carbonate, because in its presence the residue may be removed more readily from the crucible.

[2] A distinctly perceptible mirror may be obtained even from a quantity of arsenious sulphide corresponding to 0·01 mg. of arsenic trioxide (W. Fresenius, *Zeitsch. anal. Chem.*, **20**, 531).

a quite slight yellow precipitate of arsenious sulphide may be formed;[1] if traces of antimonite ion had been present in the solution of the fused mass in water, the precipitate would have been orange-coloured and insoluble in ammonium carbonate solution. When all the soluble salts have been extracted from the fused mass, any metallic residue which may have been left is examined for traces of tin and antimony (for only traces of these two metals can be present if the procedure described was exactly followed). If such traces are at all considerable, a corresponding correction must be made in the gravimetric estimation of the arsenic.

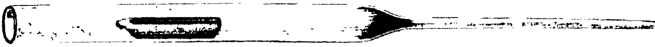

FIG. 52.

8. *Examination of the reserved residues for other metallic poisons of the second, fifth, and sixth groups.*

313. (*a*) *Residue I.* (*cf.* (301)).

This may contain, in particular, silver chloride, mercury[2] mercuric sulphide,[2] mercuric albuminate,[2] and lead sulphate, possibly also lead chloride, bismuthyl chloride, metastannic acid, and barium sulphate.

To determine first whether the residue contains mercury or its compounds, a portion of it is well mixed and thoroughly dried, treated with red fuming nitric acid, heated with it for some time, evaporated to a small residue, this residue treated with water to which a little nitric acid has been added, and the liquid allowed to cool, filtered, diluted, and treated with hydrogen sulphide. If a black precipitate is obtained, it is filtered off and tested according to (133) to see whether it is mercuric sulphide or whether it contains mercuric sulphide, possibly in addition to bismuth or lead sulphide. If mercury is present, the whole of the residue must be treated in the same way as the sample, if the metals are to be determined quantitatively. In that case, bismuth and lead, if found, must also be determined in the solution obtained by heating the mercuric sulphide with nitric acid.

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[1] In the reduction of a quantity of arsenious sulphide corresponding to 1 mgrm. of arsenic trioxide, W. Fresenius did not obtain any perceptible precipitate in the solution of the residue (*Zeitsch. anal. Chem.*, **20**, 533).

[2] *Cf.* footnote on p. 742.

The residue, free or freed from mercury, is calcined in a porcelain dish, the carbon burned with the aid of a little ammonium nitrate, the residue completely extracted with water, and the insoluble portion dried and fused with sodium carbonate and potassium cyanide in a porcelain crucible. When cold, the mass is taken up with water, the residue treated with dilute acetic acid in order to extract any barium carbonate formed, the insoluble residue, which generally remains, heated with nitric acid, and the nitric acid solution examined as in (109); any residue, insoluble in nitric acid, which is left is tested according to Sec. 179. The aqueous extract of the mass fused with potassium cyanide is acidified with nitric acid If a turbidity occurs, it is allowed to subside, the deposit filtered off and tested for silver [1] as in Sec. 70, 13, since traces of silver may have dissolved in the solution containing potassium cyanide. A portion of the acetic acid solution obtained is treated with hydrogen sulphide, in order that traces of lead may not be overlooked, and the remainder (or the liquid filtered from any separated lead sulphide) tested for barium ion by means of calcium sulphate.

(*b*) *Residue II.* (*cf.* (303)). **314.**

The carbonised residue obtained in the purification of the crude hydrogen sulphide precipitate by means of nitric and sulphuric acids, which may in particular contain compounds of lead,[2] mercury,[3] and tin, also of bismuth and antimony, and barium sulphate, is gently and continuously heated with *aqua regia*. After filtration, the residue is washed with water to which a little hydrochloric acid has first been added. The filtrate, diluted with the washings, is treated with hydrogen sulphide, and any precipitate formed examined as in Sec. 166 *et seq.*; the residue insoluble in aqua regia is calcined, the ash fused with sodium carbonate and potassium cyanide, and the fused mass tested as in (313).

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[1] With regard to special methods for the detection of *silver* in animal substances, see Nickles, *Zeitsch. anal. Chem*, **2**, 144 (1863); V. Lehmann, *Ibid.*, **21**, 470 (1882).

[2] With regard to special methods for the detection of lead in animal substances, *cf.* A. Gusserow, *Zeitsch. anal. Chem*, **1**, 120 (1862); V. Lehmann, *Ibid.*, **21**, 470 (1882).

[3] With regard to special methods for the detection of *mercury* in animal substances, *cf.* L. Riederer, *Zeitsch. anal. Chem.*, **7**, 517; Mayençon and Bergeret, *Ibid.*, **13**., 103; E. Ludwig, *Ibid.*, **17**, 395; **20**, 475; and **30**, 654; A. Mayer, *Ibid.*, **17**, 402; P. Fürbringer, *Ibid.*, **17**, 526; V. Lehmann, *Ibid*, **21**, 470; and **23**, 109; H. Paschkis, *Ibid.*, **22**, 295; Wolf and Nega, *Ibid.*, **26**, 116; Merget, *Ibid.*, **29**, 113; E. Ludwig and E. Zillner, *Ibid.*, **30**, 258; Alt, *Chem. Zentr.*, 1887, 1573; Brugnatelli, *Ibid.*, 1889, II., 614; D. Vitali, *Zeitsch. anal. Chem.*, **36**, 212; M. T. Lecco, *Ibid.*, **49**, 283; P. A. Raaschou, *Ibid.*, **49**, 172.

If *lead* is found in foods, it should be noted that water supplies may sometimes contain lead.[1]

315. (*c*) *Residue III.* (*cf.* (309)).

The precipitate insoluble in ammonium sulphide solution must be tested for the metallic poisons of the fifth group, as in Sec. 168. If a sample of the precipitate, examined spectroscopically, showed the thallium line, the precipitate should also be examined for *arsenic* (310); in that case, arsenate ion dissolves when the precipitate is heated with nitric acid, and may be precipitated by means of ammonium molybdate (Sec. 90, 9).

If copper is found in the remains of food and in cadaveric remains, the conclusion should not be drawn without further proof that *poisoning* has taken place. The presence of copper in the objects under examination may frequently be due to the fact that it is a natural constituent of corn and bread, of vegetables and other plants, and also of the lower animals, and of the organs of warm-blooded animals and human beings. The *liver* especially contains as a rule a comparatively large quantity of copper; in adults it contains 3 to 18 mgrms. of copper in one kgrm., and the liver of a fœtus and that of a new-born child contains still more; the quantities may be considerably higher, if it is present in foods, owing to the use of copper utensils or to the intentional addition of copper salts, *e.g.* in preserving vegetables or in the preparation of bread.[2]

316. (*d*) Residue IV. (*cf.* (310)).

This may contain tin and antimony, and also a little copper. It is treated as in (123).

317. 9. *Examination of the ammonium sulphide precipitate for metallic poisons of the fourth and third groups, especially for zinc, chromium,*

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[1] Th. Paul, W. Ohlmüller, R. Heise, and Fr. Auerbach, *Zeitsch. anal. Chem.*, **46**, 66 (1907).

[2] With regard to the presence and specific detection of copper in animal substances, *cf.* Ulex, *Zeitsch. anal. Chem.*, **5**, 260, and **21**, 480; H. Lossen, *Ibid.*, **5**, 261; K. B. Lehmann, *Ibid.*, **36**, 51 (1897); L. v. Itallie and J. J. van Eck, *Arch. d. Pharm.*, **251**, 50 (1913).

and thallium.[1] The liquid filtered from the hydrogen sulphide precipitate in (302) has already been treated with ammonium sulphide solution. In this process a precipitate is, as a rule, formed, which consists of ferrous sulphide and calcium phosphate, in addition to organic compounds, but can also contain the other metal ions of the third and fourth groups, especially also zinc sulphide, thallous sulphide, and chromic hydroxide, and further—if the precipitation with hydrogen sulphide was made in too acid a solution—lead sulphide and cadmium sulphide. The liquid is filtered (a funnel provided with a glass tap being used), and the filtrate examined as in (318) ; the precipitate is washed with water containing ammonium sulphide, the tap of the funnel closed, the precipitate treated with a mixture of 1 part of hydrochloric acid and 4 to 5 parts of hydrogen sulphide water, and allowed to stand for some time. After the liquid has been allowed to drain off, the treatment with hydrogen sulphide water, containing hydrochloric acid, of any residue left on the filter is, if necessary, repeated. If the conclusion is drawn that metallic poisons of the fifth group may be present here, the liquid drained off is sufficiently diluted, hydrogen sulphide introduced into it, any precipitate formed filtered on to the filter containing the residue, and washed, and the contents of the filter tested for lead, cadmium, nickel, and cobalt. For this purpose it is dissolved by heating it with dilute nitric acid, and any lead ion present separated by evaporation with excess of dilute sulphuric acid. The filtrate is next tested by means of hydrogen sulphide, after the addition of a little hydrochloric acid, for any cadmium ion that may be present, and finally any nickel or cobalt ion present is separated by means of ammonium sulphide solution. The acid filtrate, free from nickel, cobalt, lead, and cadmium ion, is treated with ammonia solution until alkaline, and then with yellow ammonium sulphide solution and allowed to stand for 24 hours in a warm place. If a precipitate is formed, it is filtered off and washed with water containing ammonium sulphide. It is then dissolved in dilute hydrochloric acid, heated until the hydrogen sulphide has escaped, filtered, and potassium iodide solution added to a portion of it. If a pale yellow precipitate of thallous iodide is obtained, the whole of the solution must be treated with potassium iodide. The precipitate is then spectroscopically examined for *thallium*. The solution, which will now contain little if any thallium ion, is evaporated to a small residue, after the addition of a little nitric acid, and this residue tested for zinc and chromium ions as in (143) to (146).

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[1] With regard to the poisonous properties of thallium, *cf.* Lamy, *J. prakt. Chem.*, **91**, 366. For the detection of thallium in forensic cases by means of electrolysis, *cf* Marmé, *Zeitsch. anal. Chem.*, **6**, 503.

According to L. van Italie and J. J. van Eck,[1] zinc is a normal constituent of the human liver; they found 18 to 87 mgrms. of it in 1 kgrm. in the liver of adults. Zinc can also occur in foods without having been added with criminal intent. In particular, dried apple rings at one time often contained zinc.[2] Finally, zinc ion is occasionally found in drinking water, into which it has either been absorbed from the soil or in which it is present owing to the action of the water on zinc supply pipes [3]

318. 10. *Examination of the filtrate from the ammonium sulphide precipitate.* The liquid filtered from the ammonium sulphide precipitate in (317) may still contain part of, and possibly all, the chromium present, because chromic ion is not completely precipitated by ammonia and ammonium sulphide from a solution containing organic substances; it may also contain barium ion, for when a soluble barium salt is present, the residue 1 only contains a quantity of barium corresponding to the sulphate ion present in the mass, or formed on treating the mass with hydrochloric acid and potassium chlorate; and the precipitate formed by hydrogen sulphide will only contain as much barium as could be precipitated by the sulphate ion resulting from the action of air on the hydrogen sulphide. Finally, it should be remembered also to take the zinc ion into consideration here, since its precipitation by means of ammonium sulphide may have been influenced by the products of decomposition of the organic substances. In order to detect chromic and barium ion, and also to test for zinc ion, the liquid should be evaporated, with the addition of a sufficient quantity of dilute sulphuric acid, until sulphuric acid vapours escape freely. When cold, the residue should be diluted the liquid filtered, and the residue washed and the separated sulphur volatilised. Should a residue be left, it should be tested for barium sulphate (208). The sulphuric acid filtrate is neutralised with sodium carbonate, evaporated to dryness, and the residue (consisting mainly of potassium sulphate) ignited to remove the ammonium sulphate, and then fused with sodium carbonate and potassium chlorate; the aqueous solution of the fused mass is tested for *chromate ion*, and any residue which may have been left tested for *zinc*.

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[1] *Arch. d. Pharm.*, **251**, 50 (1913).

[2] R. Hefelmann, *Zeitsch. anal Chem.*, **35**, 104 (1896); K. B. Lehmann, L. Janke, P. Kulisch, C. Amthor, A. Reissmann, P. Soltsien, *Ibid.*, **38**, 723.

[3] G. Wolffhugel, *Arbeiten aus dem Kais. Gesundheitsamte*, **2**, 180 (1887); F. Schwarz, *Zeitsch. Unters. Nahr. Genuss.*, **14**, 482 (1907); R. F. Weinland, *Ibid.*, **19**, 362 (1910); K. B. Lehmann, *J. Gasbeleucht. Wasservers.*, **56**, 717 (1913).

11. *Tests for the state of combination of metallic poisons found.* If arsenic was found in (311), or ions of a metal open to suspicion were detected in the examination of the residues I., II., III., IV., or of the ammonium sulphide precipitate and the liquid which was filtered from it, tests must be made to determine the state of combination in which the metal was present in the original substance. The solution of this question is always of importance, but decisively so in the case of metals which are poisonous in one state of combination but harmless in another. This is, for instance, the case with barium, which is poisonous as barium chloride or carbonate, but harmless as barium sulphate; or with chromium, which is exceedingly poisonous in the form of chromates and dichromates, but only slightly so in that of chromic compounds. **319.**

As a rule *dialysis* affords a suitable means of solving this question. If, therefore, it was not employed between the processes A., Sec. 200, and C., Sec. 202, the reserved third of the substance should be treated according to Sec. 201, in order to obtain suitable solutions for the determination of the state of combination of any suspicious metal found. The colour of the material under examination frequently affords an indication of the *state of combination of chromium compounds*. If it is yellow to orange-red, the chromium compound was introduced as chromate or dichromate. If the substance is greenish, however, it is not a proof that chromic salt was used for poisoning—it may more probably be due to a reduction of chromates—it is, therefore, not possible in this case to form a definite conclusion.[1] Soluble chromates cannot be extracted unaltered from poisoned sausage or minced meat; if such meat is introduced into a dilute solution of potassium chromate, the latter is decolorised, the salt forming a combination with the meat.[2]

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[1] J. Gadamer, *Lehrb. d. chem. Toxikologie*, 1909, p. 250.

[2] R. Otto, *Anleitung zur Ausmittelung der Gifte*, 7th ed., p. 227 (1896).

D. *Modifications of the process described in* C.

SEC. 204.

320. Numerous modifications can, of course, be made in the process described in C., and we refrain from a detailed description, as the conditions cannot all be foreseen under which such modifications offer advantages over the methods given; one modification, however, which consists in a deviation in the method of preparing the elementary arsenic, must be pointed out.

1. The solution obtained in (310) may be tested directly in Marsh's apparatus as described in Sec. 89, 12, instead of being treated with hydrogen sulphide. Reduction by means of sulphur dioxide may be omitted in this case. If arsenic is present in any considerable quantity, a portion of the liquid (previously measured or weighed) will be sufficient to obtain distinct arsenic mirrors, and the remainder can be used for the quantitative estimation of arsenic. If, however, only minute quantities of arsenic are present, so that by degrees the whole amount of the liquid has to be introduced into Marsh's apparatus in order to obtain a distinct arsenic mirror, the quantitative estimation of arsenic must be omitted, provided the Marsh test has not been carried out from the start according to Polenske's method described in the following section. The latter procedure may, therefore, be recommended for the sake of safety in all cases. If it is thought necessary to determine definitely that the resulting mirror is actually an arsenic mirror, treatment with hydrogen sulphide, as described on p. 369, should be chosen.
2. The use of the *distillation process*, described in Sec. 197, for the detection of arsenic in textile fabrics, carpets, etc., has also been recommended repeatedly for forensic purposes. In any case, it possesses the advantage of enabling a decision as to the absence or presence of arsenic to be made comparatively quickly. In such a case the filtered solution obtained in (301) should be subjected to distillation by the method described in Sec. 197, with the addition of hydrochloric acid and ferrous chloride, and the distillation continued, with renewed addition of hydrochloric acid, so long as the liquid passing over gives (after dilution with water) precipitates with hydrogen sulphide. The hydrogen sulphide precipitates from the whole distillate are collected on a filter, treated according to (308), weighed, and then subjected to further examination by means of a reduction test as in (311).

If care has been taken that the ferrous chloride used was not only absolutely free from arsenic but also from all other impurities, the residue from the distillation may be used for tests for the remaining metallic poisons in accordance with the course described in the previous section.

E. *Process intended primarily for the detection and determination of arsenic only.*

SEC. 205.

The process which will now be described has for its sole object **321.** the detection and determination of arsenic in cadaveric remains, food, and other organic substances Only occasionally can it be extended to the detection of other metallic poisons, that is to say, when the whole of the prepared solution has not been used for the detection of arsenic. The process consists in the destruction of the organic substances by means of hot concentrated mineral acids, and in the examination of the resulting solution by Marsh's method, but under conditions in which the conversion of the arsenic present into the form of a mirror takes place quantitatively. We have used this combined method (which we will describe in detail), *e.g.* for the examination of the urine, blood, and organs of persons who have been treated with salvarsan, and have always obtained satisfactory results. Since comparatively large quantities of acid are necessary for the preparation of the solution, the purity of the reagents is a point of the utmost importance (p. 734); their preliminary examination must be carried out with correspondingly large quantities.

For the first part of the work (preparation of the solution) we use the method described by M. Kerbosch [1] If necessary, the substance is stirred with water to form a thick paste, and placed in a retort with a tubulure, made of Jena glass, which should be *at least* four times as large as the volume of the substance to be destroyed. A mixture of equal parts of concentrated sulphuric acid and nitric acid of sp. gr. 1·3 is then added (approximately as many c.c. as correspond to the weight of the dry substance in grms.). Vigorous action often begins, even in the cold, so the test should be carried out in a fume cupboard.

The retort is gently heated, preferably on asbestos wire netting, until the contents have formed a uniform mass without the liquid frothing over. A separating funnel, provided with a dropping device, is introduced into the tubulure of the retort, care being taken that the tube of the funnel is about 5 mm. from the bottom of the retort. The space between the tube and the tubulure may be closed by means of a suitably-ground stopper (Fig. 53). Nitric acid is now added, drop by drop, through the separating funnel to the contents of the retort, which are meanwhile continuously heated. The temperature and the speed at which the drops fall should be so adjusted that carbonisation does not occur, and care should be taken always to have a slight excess of nitric acid. The distilling acid is collected in a receiver. At first the action is vigorous with much frothing, but after a time the formation of froth ceases. By this means a yellow liquid is obtained, which will be covered with a clear layer of the fat present. Needless to say, this will obviously only be destroyed after it has been carbonised with sulphuric acid. The temperature is now raised, and the supply of nitric acid regulated in such a way that the fine carbon formed is at once oxidised by the nitric acid which is being added. The formation of coarse fragments of carbon should be avoided.

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[1] *Arch. f. Pharm.*, **246**, 617 (1908).

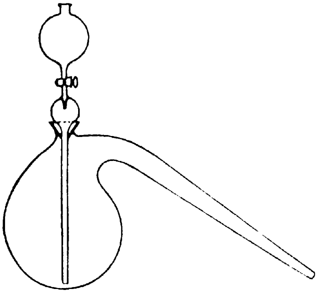

FIG. 53

In this process the layer of fat gradually disappears and a clear brown liquid will finally be present in the retort. The liquid is now strongly heated with the slow addition, drop by drop, of nitric acid until it is completely colourless, and this strong heating continued for at least an hour, in order to destroy the last traces of organic substances. In this process about 150 c.c. of acid are required for the destruction of 250 grms of fat minced meat the process is completed within 5 hours: the residue in the retort should only amount to a few c.c.[1]

322. In order to convert all the arsenic quantitatively into hydrogen arsenide in the next stage of the process, and finally to cause it to deposit in the heated glass tube in the form of an arsenic mirror, the following directions of E. Polenske [2] should be followed :—

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[1] With regard to a proposal made by Lockemann for the destruction of organic substances, *cf. Zeitsch. anal. Chem.*, **51**, 717.

[2] *Zeitsch anal. Chem.*, 39, 663 (1900); *cf.* also the comprehensive work of Lockemann in regard to Marsh's method (*Zeitsch. anal. Chem.*, **18**, 416).

The cylindrical flask for the evolution of hydrogen should contain about 250 c.c., and be four times as high as it is wide. The liquid containing the arsenic should contain approximately 20 c.c. of sulphuric acid in 100 c.c., and the quantity of arsenic in 100 c.c. of this liquid should not exceed 4 to 5 mgrms. In order to keep the sulphuric acid at the necessary strength, the residue which remained in the retort after the process just described is *very carefully* rinsed with water, when cool, and placed in a *weighed* porcelain dish, and this heated on a sand bath, in order to remove the nitric acid completely, until about one-third of the sulphuric acid has evaporated. The nitric acid is not always completely removed by a single evaporation; it is therefore necessary, when cold, to dilute it again with 50 c.c. of water and to repeat the concentration and evaporation. This is repeated until a small drop of the liquid, after dilution with water, no longer gives a reaction for nitrate ion with diphenylamine.

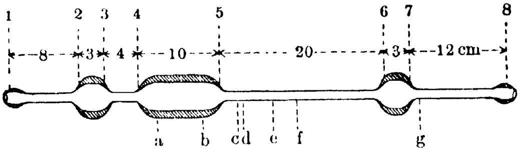

FIG 54

When this point has been reached the contents of the dish, when cold, are made up to 36 grms. with concentrated sulphuric acid, and, after being rinsed in a measuring flask, diluted to 100 c.c. with water. A portion of this solution is introduced into a burette with a glass tap, from which it is allowed to drop into the flask for the evolution of hydrogen.

This latter flask, the dimensions for which were given above, is provided with a dropping funnel, reaching nearly to the bottom of the flask, and an outlet tube for the gas. This tube is connected with a washing flask containing a 5 per cent. lead nitrate solution, and then with a **U**-tube, one half of which is filled with about 20 grms. of fused calcium chloride, and the other with caustic alkali; to this is attached an ignition tube of hard glass (Fig. 54), the other end (8) of which is connected with a small glass tube which is immersed to the depth of a few centimetres in an approximately one per cent. solution of silver nitrate. The diameter of the ignition tube is 10–12 mm. in its wider and 1·5 to 2 mm. in its constricted parts.

The zinc is first treated in the cylindrical evolution flask with about 5 c.c. of concentrated sulphuric acid and then 20 c.c. of water added; after about 15 minutes the air will have been expelled from the apparatus. For the purpose of testing the zinc and sulphuric acid, the tube is heated with a flame at *b* for half an hour, during which time, if the evolution of gas is too weak, a mixture of one volume of sulphuric acid and four volumes of water is added drop by drop. If at the end of this time no visible deposit can be seen in the tube, the reagents are sufficiently pure. The tube is now heated between 6 and 7 with one, and between 4 and 5 with two Bunsen burners with chimneys (an asbestos screen being placed at *g* and *c*), and a quarter of the liquid (25 c.c.), prepared for examination, made to drop (about 0·75 c.c. per minute) from the burette through the funnel into the evolution flask. The evolution of gas must take place steadily, and at such speed that it is possible to count the successive bubbles in the lead nitrate or silver nitrate solution through which the gas has to pass.

If no visible mirror is formed beyond *c* in this process, no arsenic is present; if, on the other hand, the solution contains too much arsenic, the silver solution is reduced. Despite this fact, the examination is carried to completion, by allowing the liquid to drop as slowly as possible and weighing the mirror in the method described below. An approximate estimation of the amount of arsenic present is thus obtained, and the remainder of the solution, prepared for examination, further diluted with dilute sulphuric acid (one volume of acid and four volumes of water) in such a way that only 4 to 5 mgrms. can still be contained in 100 c.c. The test is then repeated with *this* liquid.

When there is a steady evolution of hydrogen arsenide, the rest of the liquid is gradually added, and the flask finally rinsed with sulphuric acid which has been diluted in the proportions mentioned above. If the evolution of gas becomes too vigorous at times, it may be regulated by allowing the drops to fall at longer intervals, or by stopping the dropping for a little while. Towards the end of the test the evolution flask should be put into warm water, so that the evolution of gas is not disturbed by the separation of crystals of zinc sulphate.

By this means the whole of the arsenic will be found beyond *c* after about 2 to 2½ hours, whilst only a small mirror will appear behind *g*. The evolution of gas is maintained for about an hour, the flames then removed, and the ignition tube heated with a flame between 2 and 3. If, after a quarter of an hour, no mirror is visible beyond 3, the test is complete; if, on the other hand, a mirror appears, it should be driven along to *d* by the necessary adjustment of the flame, and the test repeated with renewed heating between 2 and 3 until no arsenic mirror appears beyond 3. If, after half an hour, only a faint yellowish-brown deposit is formed, these traces of arsenic may be ignored.

When it is certain that the arsenic has thus practically been completely expelled, the flame and the silver solution are removed and the ignition tube connected in the reverse direction at 8 with the **U**-tube, and heated by means of a small flame in a current of hydrogen until all the arsenic has been driven along to *c*. When cold, the portion of the tube *c* to *f* is cut out by means of a file (carefully, to prevent splinters of glass getting into it or particles of arsenic from being lost), and this small piece of tube, together with the arsenic in it, weighed. The latter is dissolved in concentrated nitric acid while being heated, and the tube washed out, dried and weighed again under the same conditions, so that the quantity of arsenic is obtained from the difference. If a *micro-balance* is used, even very small quantities of arsenic may be accurately determined.

Instead of such a gravimetric process, *W H. Bloemendael uses a volumetric process for the quantitative determination of arsenic separated in the form of a mirror.*[1] The arsenic mirror is dissolved in a carefully-measured quantity of a potassium dichromate sulphuric acid solution of a known normality. The liquid is then treated with potassium iodide, and the separated iodine titrated with sodium thiosulphate. By this means the quantity of potassium dichromate necessary for the oxidation of arsenic to arsenate ion, and consequently the amount of arsenic in the mirror is obtained: **323**

$$6As+5K_2Cr_2O_7+20H_2SO$$
$$=6H_3AsO_4+5K_2SO_4+5Cr_2(SO_4)_3+11H_2O$$

As a rule, $\frac{1}{100}$-*N*-sodium thiosulphate solution is used for the purpose; in the case of quantities of 0·01 mgrm. and less, Bloemendael used $\frac{1}{1000}$-*N*-sodium thiosulphate solution. We have had no personal experience with *this* form of determination.

In any case, it is essential in the procedure described in this section that certainty be obtained as to whether the mirror which appears is actually due to arsenic. Polenske's method[2] is to precipitate the arsenate ion as ammonium magnesium arsenate by means of ammonia solution and magnesia mixture from the solution of the mirror, after complete oxidation with a few drops of fuming nitric acid, with the aid of heat; the nature of the precipitate can be confirmed by means of the silver nitrate reaction.

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[1] *Arch. f. Pharm.*, **246**, 604 (1908).

[2] *Zeitsch. anal. Chem.*, **39**, 665 (1900).

If the whole of the sulphuric acid solution of arsenic present at the beginning (and since increased to 100 c.c.) has not been used, the remainder can be used for testing for other metallic poisons.

II. Process for the Detection of Hydrocyanic Acid.

Sec. 206.

824. If poisoning with hydrocyanic acid or with alkali cyanides[1] (which have the same action as hydrocyanic acid, and, owing to their being used for many technical purposes, are more easily obtained) is known or presumed to have occurred, and if the hydrocyanic acid is to be detected in food or in the contents of a stomach, the first essential is to begin the examination speedily. The reason for this is that hydrocyanic acid, being an unstable substance, may rapidly undergo decomposition,[2] and also because, in the opinion of many chemists, at all events, cyanogen compounds may be produced in the putrefaction of animal substances, although this view cannot yet be regarded as definitely proved.[3] *The period of time* during which the poison can be detected depends upon its quantity and the stage of putrefaction. On the average, the detection is still possible 9 to 10 days after the poisoning, in the lungs even after 14 days, and in the large intestine after 15 days. In the case of a dead body in good preservation it is said to be possible to detect the poison after 3½ months (J. Gadamer), and, according to Jollyman,[4] even after 6 months. If the portions of the body have been preserved with alcohol it is possible, according to G. Calvi and M. Malacarne,[5] to detect hydrocyanic acid after a month. In examining a body not only the stomach and intestinal canal, but also the blood, heart, brain, lungs, liver, and urine must be taken into consideration.

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[1] The technical "potassium cyanide" manufactured by the newer process is a mixture of potassium and sodium cyanides, or, if prepared by the Castner process, it consists only of sodium cyanide.

[2] The decomposition of hydrocyanic acid in dead bodies may take place with varying speed, but, as a rule, it continues for a considerable time, until the whole of the hydrocyanic acid is introduced into the organism and has been decomposed. *Cf.* on this question Dragendorff, *Die gerichtlich-chemische Ermittelung von Giften*, 3rd ed., Göttingen (Vandenhoek & Ruprecht), 1888, p. 59; Buchner, *J. prakt. Chem.*, **104**, 388; Bonjean, *Pharm. Zentralh.*, 1871, p. 199; H. Struve, *Zeitsch. anal. Chem.*, **12**, 15 and 19; Rennard, *Ibid.*, **13**, 110; Reichard, *Arch. d. Pharm.*, **219**, 204; Sokoloff, *Zeitsch. anal. Chem.*, **14**, 423.

[3] With regard to this question, see Taylor in Dragendorff's work, *loc. cit.*, p. 59; Bonjean, *Pharm. Zentralh.*, 1871, p. 199; W. Preyer, *Zeitsch. anal. Chem.*, **12**, 23.

[4] *Zeitsch. anal. Chem.*, **46**, 550 (1907). *Cf.* also W. Autenrieth, *Ibid.*, **50**, 536.

[5] *Ibid.*, **48**, 519 (1909).

Since, apart from the poisonous cyanogen compounds, among which hydrocyanic acid and potassium and sodium cyanides must be regarded as the most important, there are also non-poisonous compounds, of which potassium ferro- and ferricyanides and Prussian blue are the best known; and since the action of even weak acids on the latter converts a portion of their cyanogen constituent into hydrocyanic acid, it is necessary in the first place to make a few preliminary tests to determine which method should be chosen for the separation of hydrogen cyanide, in order to be able to decide with certainty whether hydrocyanic acid or alkali cyanide was originally present.

A. *Preliminary Tests.*

1. The odour of the substance under examination is carefully **325.** noted. Hydrocyanic acid may be recognised at once, if present in any considerable quantity in substances free from other odorous compounds. If, however, cadaveric remains under examination are already in process of putrefaction, the odour of hydrocyanic acid may be masked by that of the putrefying substances. The odour alone, however, must never be regarded as a sufficient proof of the presence of hydrocyanic acid, for benzaldehyde and nitrobenzene have, to some extent, similar odours.

2 A little of the substance, with the addition of water, if necessary, **326.** is placed on a moistened filter, and the filtrate collected, acidified with hydrochloric acid, and tested for ferrocyanogen ion with ferric chloride, and for ferricyanogen ion with ferrous sulphate. Any soluble thiocyanates present would also be found in the former test. If a ferrocyanogen, ferricyanogen, or thiocyanogen compound has been found, the greatest care will be required for the detection of any simple cyanogen compounds (hydrogen cyanide, alkali cyanide) in the presence of these compounds. The examination is continued at B. 2 (331).

Since potassium ferrocyanide and potassium ferricyanide are decomposed even in cold aqueous solution, and more rapidly in acid or hot solutions, the conclusion that there has been hydrocyanic acid or alkali cyanide poisoning, when hydrocyanic acid has been found in a dead body, in addition to ferrocyanogen or ferricyanogen compounds, is never justifiable, according to Almén,[1] whilst according to R. Fresenius [2] it is only permissible under certain conditions, as, for example, when a relatively large amount of hydrocyanic acid with little potassium ferrocyanide is found in a body a short time after death.

327. 3. If ferro- or ferricyanogen compounds and thiocyanogen compounds have not been found, a preliminary test is next made with guaiacum paper containing copper sulphate. For this purpose the reaction of the substance, which, if not fluid, must be treated with a little water, is determined. If the reaction is acid, the substance is suitable for the test at once, but if it is neutral or alkaline, it should be acidified with tartaric acid solution The air in the flask above the substance under examination is then tested by suspending in it guaiacum paper containing cupric sulphate, as in Sec. 120, 11. If the paper turns blue it is presumptive evidence, but not conclusive proof, of the presence of hydrocyanic acid or alkali cyanide. Mercuric cyanide, if present, would not give the reaction. The examination is continued at B. 1 (329).

328. 4. If the preliminary tests in 1, 2, and 3 have given negative results, mercuric cyanide may still be present. The examination is continued at B 3 (333).

B. *Separation and detection of hydrocyanic acid or of cyanogen in poisonous cyanides.*

329. 1. If the preliminary test (A. 2) has shown that ferro- and ferricyanogen compounds, and also thiocyanogen compounds are absent, and if the guaiacum paper has turned blue (A. 3), the substance under examination is mixed with water, if necessary, and, if it does not show a strongly acid reaction, is treated with tartaric acid solution until it reddens litmus paper strongly. It is then introduced into a distillation flask, which must not be too large, and this is connected by means of a tube passing through its cork with an inclined condenser. The lower end of the condenser tube passes through an opening in the cork of a graduated cylinder (which serves as a receiver), so as to form an air-tight joint, whilst this cylinder is attached, by means of a tube passing through a second opening in its cork and bent twice at right angles, to a **U**-tube (Péligot tube). The latter is charged with a very dilute solution of sodium hydroxide, which is known to be free from cyanide.[1] The flask is carefully heated in an oil bath or calcium chloride bath, the bottom of which it must not touch, in such a way as to avoid *excessive heating* of the sides of the vessel,[2] and so that the contents continue gently boiling.

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[1] *Chem. Zentr.*, 1872, p. 439.

[2] *Cf.* also Ludwig and Mauthner, *Zeitsch. anal. Chem.*, **20**, 604 (1881).

As soon as about 12 c.c. have distilled, the cylinder is removed, and replaced by a weighed boiling flask of larger capacity, which must also be connected with the U-tube mentioned above. Sometimes, especially when there is much frothing, it is advisable to make the distillation in a *current of steam*. The steam for this purpose is conducted to the bottom of the flask, the steam generator consisting of a large flask in which water is boiled during the distillation, and which is provided with a glass tube bent twice at right angles, the delivery end of which passes through a second opening in the cork of the distillation flask.

330. The first distillate is measured or weighed, and tested as follows:

(*a*) One quarter is treated as in Sec. 120, 8, to convert the hydrocyanic acid into the form of *ferric thiocyanate*. Since it may easily happen that the distillate contains acetic acid, care should be taken to add some additional hydrochloric acid to counteract the injurious influence of the ammonium acetate.

(*b*) Another quarter is treated as in Sec. 120, 7, to convert the cyanogen ion of the hydrocyanic acid into Prussian blue.

(*c*) If the tests (*a*) and (*b*) have proved with certainty that hydrocyanic acid is present, the remaining half of the distillate is used for a quantitative estimation thereof. If, however, one of these reactions has failed to give a decisive result, a further quarter of the distillate is used for the reaction described in Sec. 120, 9, depending upon the conversion of hydrocyanic acid into *nitroprusside ion*, whilst the quantitative estimation is made in the last quarter.

(*d*) In making an approximate *quantitative estimation*, the distillation is continued so long as a liquid containing hydrocyanic acid distils, the distillate mixed with the contents of the **U**-tube, and a half (or a quarter) of this liquid mixed with half (or a quarter) of the distillate first collected in the cylinder. If the mixture is not already acid, sufficient tartaric acid to produce an acid reaction is added, and it is then introduced into a retort or distillation flask, treated with borax or sodium hydrogen carbonate to retain the hydrochloric acid, and distilled down to a small residue. The distillate thus obtained, which will contain the whole of the hydrocyanic acid and be free from hydrochloric acid, is treated with silver nitrate solution, then with ammonia solution in excess, and lastly with nitric acid until the reaction is strongly acid. The resulting precipitate of silver cyanide is allowed to subside, collected on a filter paper (which has previously been dried at 100° and weighed), washed, dried at 100°, and weighed. The weight multiplied by 0·2017 gives the corresponding quantity of anhydrous hydrocyanic acid, and the result multiplied by 2 or by 4 (according to whether a half or a quarter of the liquid was taken for the estimation) gives the entire quantity of hydrocyanic acid originally present or formed by the decomposition of alkali cyanide.

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[1] If it is necessary to combine the examination for hydrocyanic acid with tests for phosphorus, the receiver of the apparatus described in (336) must be included, and the distillation carried out in the dark.

[2] Ganassini, *Zeitsch. anal. Chem.* (1907), **46**, 549.

331.2. If the preliminary examination has indicated the *presence* of complex cyanogen ions (ferrocyanogen, ferricyanogen, and thiocyanogen compounds), the method described in 1 (329) cannot be used for the separation of hydrocyanic acid, because tartaric acid would liberate hydrocyanic acid from the practically non-poisonous compounds mentioned, at the boiling temperature of the liquid. Hence one of the following methods must be chosen:—

(*a*) *Methods which are applicable in the presence of either ferro- or ferricyanogen compounds or of thiocyanogen compounds.* The following method, devised by Jacquemin,[1] is based upon the fact that hydrocyanic acid can be expelled from *alkali hydrogen carbonate solutions*, whereas no hydrocyanic acid is liberated from complex cyanogen ions in such solutions *so long as the temperature does not exceed* 60°. This has been confirmed by later experiments of A. Hilger and K. Tamba,[2] and of H. Beckurts and W. Lehrmann.[3]

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[1] *Ann. chim. phys.* (5), **4**, 135.

[2] *Zeitsch. anal. Chem.*, **30**, 529 (1891).

[3] *Zeitsch. Unters. Nahr. Genuss.*, **3**, 415 (1900).

The latter, in particular, have shown that whereas no hydrocyanic acid is liberated from 1 per cent. solutions of potassium ferrocyanide, traces are liberated from 2 per cent. solutions, whilst the distillate from 5 per cent. solutions will contain appreciable quantities of hydrogen cyanide if the liquid is heated above 60°. In applying the test the directions of R. Otto[1] and G. Baumert[2] are followed, according to which the substance under examination is diluted with a sufficient quantity of water and mixed with a moderate quantity of sodium hydrogen carbonate in a flask, the cork of which has three openings. Through the centre opening is passed a thermometer which reaches nearly to the bottom of the flask, whilst the usual inlet and outlet tubes are passed through the other two openings. Washed carbon dioxide is admitted through the inlet tube, which also extends to the bottom of the flask, whilst the outlet tube leads to a condenser with which are connected the vessels used as receivers, in the same way as described in (329). The liquid is distilled on the water bath, care being taken to maintain the temperature rigidly within the limit mentioned, and the distillate is treated as in (330).

In the case, which in practice hardly ever occurs, of its being necessary to test not only for hydrocyanic acid and alkali cyanides, but *also for phosphorus* in the presence of complex cyanides, only a small quantity of the liquid should be distilled, and the residue in the distillation flask again acidified, and tested for phosphorus by Mitscherlich's method (336) (R. Otto).

(*b*) *Methods which are suitable for eliminating the disturbing influence of ferro- or ferricyanogen compounds, but not that of thiocyanogen compounds.* The substance under examination is diluted with water if necessary, rendered slightly acid with tartaric acid, and vigorously shaken with an equal volume of ether. After separation of the ethereal layer, the shaking with ether is repeated. The united ethereal extracts will be free from hydroferrocyanic and hydroferricyanic acids, but will contain hydrocyanic acid originally present and that liberated from alkali cyanides. The free hydrocyanic acid may now be separated from the **332.**

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[1] *Anleitung zur Ausmittelung der Gifte*, 7th ed., p. 34 (1896).

[2] *Lehrbuch der gerichtlichen Chemie*, **1**, 2nd ed., 259 (1907).

ethereal extract by shaking the latter with water containing sodium hydroxide, and may be detected in the aqueous extract as in Sec. 120, 7, 8, and 9 (Barfoed,[1] Beckurts and Schönfeldt).[2] This method cannot be recommended when mercuric cyanide is present, because, although this compound is extracted when its aqueous solution is shaken with ether, it is only dissolved to a limited extent, and its complete extraction is difficult; in this case the method given in (333) is used.

333. 3. The extremely poisonous *mercuric cyanide* yields a distillate containing hydrocyanic acid only when a considerable quantity of the compound is present. If, however, a smaller quantity is present in dilute solution, no trace of hydrocyanic acid is distilled, even when the liquid has been strongly acidified with tartaric acid; but on adding a few c.c. of fresh hydrogen sulphide water and repeating the distillation, the mercuric cyanide will be completely decomposed, and the distillate will contain hydrocyanic acid (W. Autenrieth).[3] Mercuric ion will be found as mercuric sulphide in the residue from the distillation

According to Autenrieth,[4] mercuric cyanide may be detected in the presence of complex cyanogen ions as in (331) if the liquid to be distilled is treated with sodium hydrogen carbonate in not too small a quantity, and a few c.c. of freshly prepared strong hydrogen sulphide water are added.

Mercuric oxycyanide may be detected in the same way as mercuric cyanide by means of this method; the commercial preparations of this compound, which has recently been occasionally used in medicine, usually contains considerable proportions of mercuric cyanide.[5]

If the ethereal extract obtained as described in (332) contains mercuric compounds in addition to hydrocyanic acid, it does not necessarily follow that mercuric cyanide was present, since other mercuric salts, especially the chloride, are also soluble in ether (Gadamer). The presence of mercuric cyanide (or of mercuric oxycyanide) can only be regarded as definitely proved when the tests for hydrocyanic acid in (329) and (331) have given negative results, and that in (333) a positive result; whilst, in addition to this, mercuric ion has been found in the distillation residue. In any case, however, it must be remembered that mercuric cyanide is always formed when mercuric and cyanogen ions come in contact.

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[1] *Lehrbuch der organischen qualitativen Analyse*, p 169 (1881).

[2] *Zeitsch. anal. Chem.*, **23**, 117 (1884).

[3] *Die Auffindung der Gifte*, 4th ed., p. 24 (1909).

[4] *Arch. d. Pharm.*, **231**, 107 (1893).

[5] E. Rupp, *Arch. d. Pharm.*, **246**, 470 (1908).

III. Method for the Detection of Ordinary Phosphorus.[1]

SEC. 207.

Since the use of white or yellow phosphorus for the manufacture **334.** of wooden and other matches was prohibited in Germany by an Imperial statute of May 10th, 1903, to come into force on Jan. 1st, 1907, cases of phosphorus poisoning have been decidedly less frequent than formerly, when the material was particularly easily accessible in the form of phosphorus matches. But phosphorus pastes and pills for poisoning rats and mice and drugs containing phosphorus (phosphorised oil and cod liver oil) may still be procured without difficulty, so that, even at the present time, the chemist is not infrequently set the task of detecting phosphorus in the contents of the stomach or in food. In such examination it is of primary importance that his sole aim must be to separate the phosphorus in the free condition, or to bring about reactions which depend upon the presence of *ordinary* (*colourless, white*, or *yellow*) phosphorus, for the detection of *red* or *light red* phosphorus, or of phosphorus in the form of phosphates, would be devoid of all significance, inasmuch as the former is non-poisonous, and the latter are of normal occurrence in animal and vegetable organisms.

Since any free phosphorus present is converted by the action of the air first into phosphorous acid and eventually into phosphoric acid, which compounds no longer allow of any conclusion being drawn as to whether free phosphorus was originally present, it is essential that any unnecessary delay should be avoided. Since, however, particles of phosphorus enveloped in viscid organic substances require a fairly long time before they are completely oxidised to phosphoric acid, the detection of free phosphorus in cadaveric remains is often successful, even when the examination has not been made until several weeks after death (Neumann,[2] Dragendorff,[3]

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[1] Since only ordinary (colourless, white, or yellow) phosphorus is poisonous, whilst red or light red phosphorus is not poisonous, the term "phosphorus" in the following section always means ordinary phosphorus.

[2] Taylor-Seideler, *Gifte*, II., p. 179.

[3] Dragendorff, *Die gerichtlich-chemische Ermittelung von Giften*, 3rd ed., p. 99 (Vandenhoek & Ruprecht, Gottingen, 1888).

Fischer and J. Müller,[1] Elvers,[2] Medicus [3]). Phosphorus present in food in the proportion of 3 mgrms. in 120 grms. could still be detected after 140 days; any material diminution in the amount of phosphorus only occurred so long as the mass was still moist and spongy, whilst, after drying, only slight oxidation continued (Nattermann and Hilger). In the examination of dead bodies the trustworthiness of the results may, according to the repeated experiments of Selmi,[4] be influenced by the fact that by the putrefaction of albumin, brains, and even of parts preserved in spirit, especially viscera, there may be formed volatile substances containing phosphorus, which are readily soluble in ether and carbon bisulphide, and turn a solution of silver nitrate brown.

In examining dead bodies not only the contents of the stomach and intestines, but also the liver, brains, and blood have to be taken into consideration. Since the brain substance is itself rich in phosphorus, and putrefied brain, when distilled with water, may yield a distillate containing phosphorus, it is advisable to make a separate examination of the brain. In addition to the cadaveric remains, any vomit, fæces, or urine [5] present should also be examined. Since the unpleasant odour which phosphorus, even in very minute quantities, imparts to food and drink gives a warning of its presence before they are taken, the detection of phosphorus is, in most cases, confined to the examination of remains of food in cases of attempted poisoning, and is but seldom required in connection with cadaveric remains.

A. Detection of Unoxidised Phosphorus.

1. Preliminary Examination.

335. A test should first be made whether the substance under examination does not show by its odour or by phosphorescing in the dark that it contains unoxidised phosphorus, and to this end care should be taken to bring the phosphorus enveloped in the mass into increased contact with the air by rubbing, stirring, or shaking. Luminescence in the dark is not an absolute proof of the presence of phosphorus, since there are also many other causes of such phosphorescence phenomena. A further examination must, therefore, always be made, beginning with the following preliminary tests :—

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[1] *Zeitsch. anal. Chem.*, **15**, 57.

[2] *Chem. Zentr.*, 1877, 70.

[3] *Zeitsch. anal. Chem.*, **19**, 164.

[4] *Ber.*, **9**, 1127, and **11**, 1691.

[5] With regard to the characteristic nature and distinctive behaviour shown by urine in cases of phosphorus poisoning, see Selmi, *Zeitsch. anal. Chem.*, **14**, 232, and **21**, 481; v. Mering, *Ibid.*, **15**, 507; Pesci and Stroppo, *Pharm. Zentralh.*, 1880, 166.

(*a*) A portion of the substance is stirred in a flat porcelain dish, which is heated on a water bath in the dark. Luminescent particles are then picked out, and may be subjected to further tests.

(*b*) A little of the substance under examination is examined by J. Scherer's method,[1] in which it is stirred with water, acidified with sulphuric acid, and introduced into a small flask, in the neck of which are suspended, by means of a loosely-inserted cork, two strips of filter paper, one saturated with silver nitrate solution and the other with lead acetate solution, and both of which have been dried with filter paper after saturation. The strips must not touch each other. The flask is then heated at 30° to 40° for a long time (up to 24 hours) *in the dark*. If only the silver nitrate paper has then become blackened, the presence of free phosphorus is indicated ; if both strips have been blackened, hydrogen sulphide may be the cause ; but if the silver nitrate paper remains white, free phosphorus is certainly not present. As a confirmatory test, the silver nitrate paper, if blackened, is oxidised with *aqua regia* and extracted with water, and the extract evaporated and finally tested for phosphate ion by means of ammonium molybdate. It is essential to make a blank test to prove that any positive result obtained is not due to the presence of phosphate in the paper. To eliminate blackening of the silver nitrate paper by hydrogen sulphide, a sulphuric acid solution of 2 to 3 grms. of cadmium sulphate may be added to the mass ; on the other hand, an addition of lead acetate must be avoided, since it has an influence on the phosphorus reaction of the silver nitrate paper.[2] Inasmuch as positive reactions were obtained by R. Fresenius and C. Neubauer[3] with formic acid, and by H. Nattermann and A. Hilger with beer and milk free from phosphorus, Scherer's method is a proof of the absence rather than of the presence of free phosphorus. In the former case, however, it is very sensitive. If free phosphorus has not been proved to be absent by this test, the main portion must be examined by one of the following methods :

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[1] *Ann. d. Chem. u. Pharm.*, **112**, 216.
[2] E Rupp, *Zeitsch. Unters. Nahr. Genuss.*, **3**, 415 (1900).
[3] *Zeitsch. anal. Chem.*, **1**, 338 (1862).

2. Actual Examination.

(*a*) *By distillation with water.*

336. This excellent and trustworthy method, devised by E. Mitscherlich,[1] depends upon separating the phosphorus in a current of steam, and then causing it to phosphoresce.

A large portion of the substance under examination is treated with water and a little dilute sulphuric acid[2] or, if a simultaneous test is to be made for hydrocyanic acid, with tartaric acid, and introduced into a flask A (Fig. 55, p. 771) and gently boiled. The flask must not be too small, or its contents may froth over; and the safest method is to heat it in an oil or calcium chloride bath. The flask is connected by means of the tube *bb* (bent twice at right angles) with the vertical glass condenser B, beneath which is a flask C to receive the distillate. The test must be made in a dark room which is light-proof, and in which, of course, no artificial light must be present. In order not to be misled by reflections in observing the phenomena in the dark, the burner beneath A must be raised to its full extent, and completely surrounded by a metal cylinder, provided at the top and the bottom with slots for the necessary supply of air to the flame. It is also advisable to introduce a black screen between the flask A and the condenser B, provided with a suitable opening for the passage of the tube *bb*.

If the substance in A contains phosphorus, the most distinct phosphorescence (usually a luminous ring which rises and falls) will be observed in the dark at the point where the steam enters the upper cooled part of the condenser tube. Under these conditions it is possible to distil from 150 grms. of mass containing only 1·5 mgrms. of phosphorus, *i.e.* only 0·001 per cent., more than 90 grms., over a period of half an hour without the luminescence stopping; even when Mitscherlich interrupted the experiment after half an hour, left the flask open for 14 days, and then continued the distillation, the luminescence again appeared with undiminished intensity. H. Nattermann and A. Hilger obtained a distinct phosphorescence, which could not be overlooked, on distilling mixtures of 0·1 mgrm. of phosphorus with 100 to 200 grms. of meat or vegetable, diluted to 1 litre.

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[1] *J. prakt. Chem.*, **66**, 238.

[2] If there is reason to suppose that phosphorus may have been introduced into the substance under examination in the form of matches, H. Hager (*Zeitsch. anal. Chem.*, **10**, 255) recommends the further addition of a little ferrous chloride or sulphate to eliminate the disturbing influence of oxidising substances in the match-heads. If, in the preliminary examination (335) a reaction for hydrogen sulphide has been obtained, ferric chloride must be added to the substance to be distilled, to prevent any hydrogen sulphide passing over into the distillate.

If a mass *containing both hydrocyanic acid and phosphorus* is distilled, the former will tend to be found in the earlier portions of the distillate, and the latter in the later portions. It is, therefore, advisable, after about 15 c.c. have distilled, to change the receiver, so that any hydrocyanic acid which has distilled may not be obtained in too dilute condition; care must also be taken in such cases to attach the lower end of the condenser to the receiver by means of a

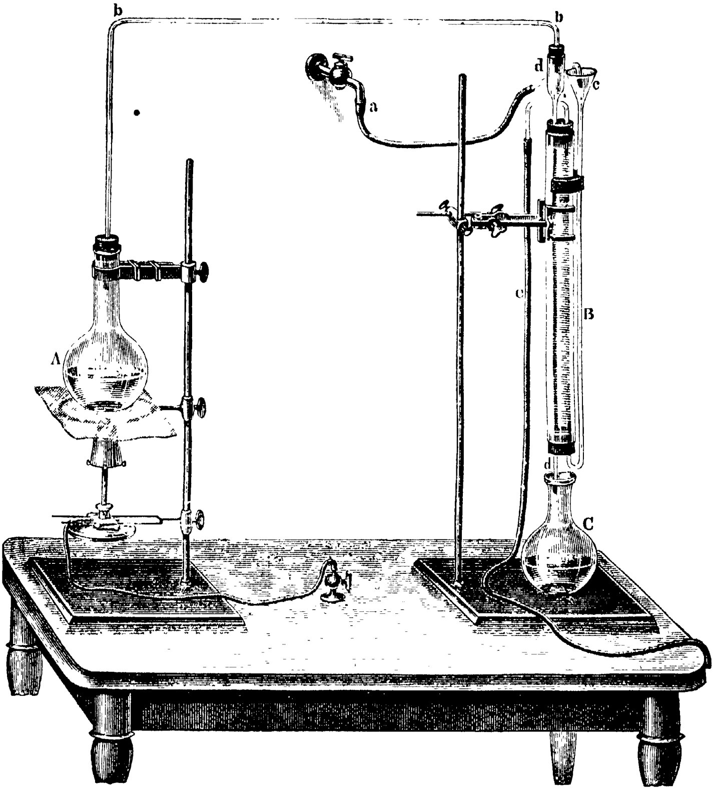

Fig. 55.

perforated cork, and also to connect a U-tube, charged with sodium hydroxide free from cyanide, with the receiver (329).

337. If the liquid contains *substances which prevent the phosphorescence*, such as ether, alcohol, petroleum spirit, phenol, cresol, chloroform, oil of turpentine,[1] and many other essential oils, no luminescence will occur so long as these continue to distil. Since, however, ether and alcohol are rapidly distilled, phosphorescence will soon be observed when they alone are present; oil of turpentine and other essential oils, however, inhibit phosphorescence permanently.[2] Free sulphur does not interfere with the luminescence, but if hydrogen sulphide was present, or has been formed on acidifying the mass under examination, it must be destroyed by the addition of ferric chloride, as mentioned above, before heating the flask. Sulphur dioxide and chlorine, and also mercuric chloride,[3] prevent the phosphorescence, and even cupric sulphate has this effect if the mass is only slightly acidified (Bernbeck).

If any considerable quantity of phosphorus is present, minute globules of phosphorus will be found at the bottom of the flask which receives the distillate. In Mitscherlich's experiments a mass weighing 150 grms, and containing 0·02 grm. of phosphorus, yielded so large an amount of phosphorus globules, that a tenth of the quantity was sufficient for the identification of phosphorus. In forensic cases they should first be washed with alcohol and then weighed. A portion may then be submitted to further examination to prove definitely that it is phosphorus; the remainder, and also a portion of the liquid which shows the phosphorescence when distilled, should be reserved as exhibits in connection with the report.

The *distillation residue* left in the flask A often contains an appreciable amount of phosphorus which has not distilled. It is no longer free unchanged phosphorus, however, for the greater part has been oxidised into phosphate ion (PO_4^{III}), and smaller fractions into phosphite ion (PO_3^{III}) and hypophosphate ion (PO_3^{II}), whilst a small portion has also been converted into red phosphorus (Nattermann and Hilger).

338. The *residue* from the distillation may, if necessary, be tested for phosphite ion as in (349); in the same way further tests may be applied to the *distillate* to confirm the presence of phosphorus therein, or to detect phosphite ion formed by the oxidation of the phosphorus vapour. If, however, the distillate is to be used for a *quantitative estimation* (which will only be roughly approximate) of the phosphorus present in the free condition, the distillation should be continued until the phosphorescence stops, and the entire contents of the receiver treated with chlorine to convert the whole of the phosphorus and phosphite ion into phosphate ion, the latter estimated, after suitable concentration, by precipitation with magnesia mixture, and the amount of phosphorus, eventually weighed in the form of magnesium pyrophosphate, is doubled. Even then the quantity of phosphorus thus estimated is frequently too small rather than too large. If the apparatus used for the distillation is not unnecessarily large, and the distillation is carried out in such a way that the phosphorescence always appears in the condenser, and not in the flask or in the tube connecting it with the condenser, and is continued until no further luminescence can be observed, even in an absolutely dark room, at least a half and, under especially favourable conditions, even three-quarters of the phosphorus present in the free condition is obtained.

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[1] Oil of turpentine acts as an antidote to phosphorus poisoning.

[2] C. Stich, *Zeitsch. Unters. Nahr. Genuss.*, **6**, 657 (1903).

[3] K. Polstorff and J. Mensching, *Ber.*, **19**, 1763 (1886).

If the mass to be tested for phosphorus is of such a nature that it seems likely to cause the liquid to bump, it is advisable to carry out the distillation in a flask heated on a sand bath, and to introduce steam at a moderate tension into the flask. If the apparatus is first filled with carbon dioxide, and the distillation with steam continued sufficiently long, almost the whole of the free phosphorus present will be recovered in the receiver (M. Buchner).[1]

It should be noted that the mere detection of phosphate ion in **339.** the distillate which has been treated with chlorine or nitric acid is not an absolute proof of the presence of free phosphorus in the substance under examination, even when there is no possibility of small particles of phosphoric acid having been carried over, by spirting, into the distillate. In this connection reference may be made to the experiments of Selmi, mentioned on p. 768, and to those of H. W. Bettink and F. C. E. v. Embden,[2] who, from the cadaveric remains of a man who had taken hypophosphites as a medicine, obtained distillates in which traces of hypophosphite ion and of hydrogen phosphide were detected.

It is, moreover, of special importance that the so-called *phosphorus sesquisulphide* (P_4S_3), which since the prohibition of white phosphorus matches in Germany has been occasionally used in the preparation of the so-called Swedish friction matches, which can be struck anywhere, gives not only distillates containing the oxidation products of phosphorus, but also, on distillation, shows the same luminescence as white phosphorus. Mitscherlich's method is, therefore, only conclusive in cases where the absence of phosphorus sesquisulphide may be assumed with certainty, or where *elementary phosphorus* can be identified in that form *in the distillate*. This latter is detected by a microscopical examination, or by dissolving the substance in carbon bisulphide. In the latter test the solution, when allowed to evaporate spontaneously, leaves a residue which phosphoresces when gently rubbed in the dark (Gadamer).

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[1] *Zeitsch anal. Chem*, **14**, 165.

[2] *Chem. Zentr.*, 1893 II, 1104.

340. A sharp test for the *detection of white phosphorus in the presence of phosphorus sesquisulphide* has been based by R. Schenck and E. Scharff[1] on the fact that the vapours from the former ionise the air, whereas those from the latter do not. A current of air is passed over the substance under examination, which is heated to 50°, and then conducted into a completely closed cylindrical metal vessel (dissociation chamber), upon the cover of which is placed an insulated electroscope, from which a dissociating body extends downwards into the cylinder. If the charged electroscope shows a decrease in tension, white phosphorus was present. In this way it was possible to detect as little as 0·004 mgrm. of phosphorus; the electroscope indicated a decrease in the voltage of 0·4 to 0·5 scale divisions in 5 minutes.

(*b*) *By expelling the phosphorus in a current of carbon dioxide.*

341. During the distillation by Mitscherlich's method a very considerable amount of the phosphorus undergoes oxidation in the flask A itself (337), and therefore does not pass over into the distillate, and for this reason the quantitative estimation made, as described in (338), is very inaccurate. Since, however, the quantitative estimation of the amount of phosphorus is of great importance, J. Scherer had recommended expelling the air from the distillation apparatus and thereby preventing the oxidation. For this purpose he added to the acidified liquid in the flask A small fragments of calcium carbonate, and did not begin to heat the flask until a sufficient evolution of carbon dioxide had occurred. R. Fresenius and C. Neubauer[2] preferred to pass a current of carbon dioxide through the apparatus during the distillation. This is generated in a Kipp's generator, washed with water in a washing flask, and introduced into the flask A by means of a glass tube, which passes through the cork and reaches to the bottom of the flask.

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[1] *Ber.*, **39**, 1522 (1906).

[2] *Zeitsch. anal. Chem.*, **1**, 339.

Naturally such precautions have an influence on the phosphorescence, **342.** which is due to the oxidation of the phosphorus vapour by the atmospheric oxygen. Since, under some conditions, the phosphorescence is the only unassailable proof of identification, whilst an approximate quantitative estimation is of equal importance, attempts were made to discover the experimental conditions under which these conflicting requirements could be reconciled. This difficulty was obviated by Nattermann and Hilger[1] in the following method, in which the air is first allowed to come in contact with the phosphorus vapour in the tube *bb*. If the phosphorus has reached this point without oxidation, no further loss need be feared, for the oxidation products formed *there* will be carried forward by the condensed water into the receiver.

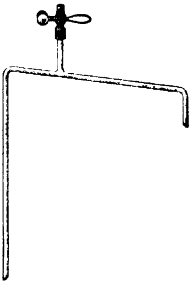

FIG. 56.

In Nattermann and Hilger's method the flask A, as shown in Fig. 55 (p. 771), is provided with a stopper with three openings. Through the first of these is passed the tube (extending nearly to the bottom of the flask) which admits the carbon dioxide from an apparatus connected with a washing flask, as in the apparatus of Fresenius and Neubauer; the second opening receives a tube, which also extends nearly to the bottom of the flask, and is connected with a steam generator, such as a small boiling flask; whilst through the third opening is passed the vertical portion of the tube *bb*, as in Mitscherlich's apparatus. This tube, however, is constructed as shown in Fig. 56, *i.e.* it has upon the portion which is slightly inclined towards the condenser a vertical branch, a few cm. in length, which can be closed by means of a rubber tube and spring clip. An Erlenmeyer flask and cylinder are used as the receivers. The former has a stopper with two openings, through one of which passes (so as to form an air-tight joint) a tube reaching to the bottom of the flask and connected at its other end with the condenser, whilst the second opening receives a U-shaped outlet tube connected with the cylinder, through the stopper of which it extends nearly to the bottom. An outlet tube passing through a second opening in the stopper of the cylinder is attached to a suction pump. A little water is placed in the Erlenmeyer flask and cylinder.

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[1] *Forschungsberichte uber Lebensmittel usw.*, **4**, 247 (1897).

After the flask A has been charged with the acidified suspension of the substance under examination, and the air has been expelled from the apparatus by means of a current of carbon dioxide, which is continued, heat is applied to the flask. As soon as the liquid begins to boil, which may be recognised in the dark by placing the hand on the vertical part of the tube *bb*, the spring clip of the branch tube is opened, and a current of air drawn through it by means of the suction pump. In the presence of phosphorus very pronounced luminescence will be observed in the narrow tube *bb*. *As soon as the luminescence has been distinctly observed*, the spring clip is again closed, the suction pump detached from the receiving cylinder, and the distillation completed in a current of steam (from the steam generator), while the current of carbon dioxide is continued to the end. Finally the contents of both receivers are oxidised in the manner described on p. 773, and the phosphate ion determined.[1] By this method it was found possible to detect 0·06 mgrm. of phosphorus, and to recover 92 to 95 per cent. of the phosphorus present.

343. More recent investigations have shown that by making the test in this way, phosphorescence takes place even in the presence of such substances as prevent it when Mitscherlich's original method is used. As a safeguard, if *no phosphorescence* has been observed either in Mitscherlich's method of applying the test or that of Nattermann and Hilger, a further portion of the substance under examination should be treated by the following method of R. Fresenius and C. Neubauer[2] before a final conclusion is formed. This is based on the fact that, on conducting the phosphorus vapour, distilled in a current of carbon dioxide, into *silver nitrate solution*, portions of it are converted into silver phosphide. The substance is introduced, with the addition of water if necessary, into a glass flask closed with a stopper having two openings. The liquid is acidified with dilute sulphuric acid, and a slow current of washed carbon dioxide from a Kipp's generator is introduced through a tube which reaches nearly to the bottom of the flask, and, escaping through the second tube at the top of the flask, passes through one or more connected **U**-tubes, which should not be too wide. These are enlarged at the base into a series of bulbs, and each is charged with not more than 50 to 60 c.c. of a neutral 3 per cent. solution of silver nitrate. When the flask is filled with carbon dioxide, it is heated on the water bath, the heating being continued for several hours. If free phosphorus is present, it will volatilise unoxidised in the current of carbon dioxide, pass into the silver nitrate solution, and cause the formation of insoluble black silver phosphide, on the one hand, and of metallic silver and phosphoric acid on the other. Since a black precipitate may also be produced (by volatile reducing substances or hydrogen sulphide) in the absence of phosphorus, the mere formation of such a precipitate is not a definite proof that phosphorus is present, but its non-occurrence proves with certainty the absence of unoxidised phosphorus.

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[1] The phosphate ion thus obtained, however, can only be regarded as definitely derived from phosphorus originally present, when no particles of the distilling liquid have spirted over, and when the substance under examination was free from putrefying brain substance (p. 768).

[2] *Zeitsch. anal. Chem.*, **1**, 340.

Any precipitate obtained is collected and washed with water on a filter which has been previously thoroughly washed with dilute nitric acid and water. Blondlot's method, improved by Dusart,[1] may be used for the detection of the silver phosphide in the precipitate. In this method the silver phosphide is decomposed by means of nascent hydrogen, with the formation of hydrogen phosphide, which is identified by its characteristic flame coloration on ignition. This further examination of the silver precipitate must be made *as soon as possible* after the precipitation is complete. A type of apparatus for the test is described by Nattermann and Hilger, and shown in Fig. 57. **344.**

A small flask *a* with a capacity of about 100 c.c. has a wide neck, into which is fitted a cork with three openings Through two of these are passed the tubes *c* and *d*, bent at right angles, which either terminate immediately below the cork, or one of which, *c*, preferably extends further down, but does not reach to the bottom of the flask. Hydrogen from a Kipp's apparatus is introduced through *c*, and then passes through *d* to the U-tube *e*, which contains fragments of pumice stone saturated with concentrated potassium hydroxide solution, and finally escapes through the glass tube *f*, which is fitted with a platinum point *f*.[2] The third opening receives the thistle funnel *b*, the tube of which reaches to the bottom of the flask *a*. The filter containing the black silver precipitate is cut up and introduced into the flask *a*; this also contains a few fragments of pure zinc and sufficient water to cover the lower end of the tube *b*, the end of *c* being left free. Hydrogen from the Kipp's apparatus is now made to pass through the apparatus, the gas ignited, *with the necessary precautions*, and a note made as to whether the flame is colourless, *i.e.* whether the zinc used is free from phosphorus. This test is rendered still more sharp by observing the flame through a spectroscope. Even the smallest traces of phosphorus are characterised by two pale-green lines (λ=526·4 and 510·7 $\mu\mu$), between which lies a faint green line. The spectrum is particularly sharp when the flame is directed against the exterior of a platinum basin filled with cold water.

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[1] *Zeitsch. anal. Chem.*, **1**, 129.

[2] In Dalmon's method (346) this platinum point is indispensable.

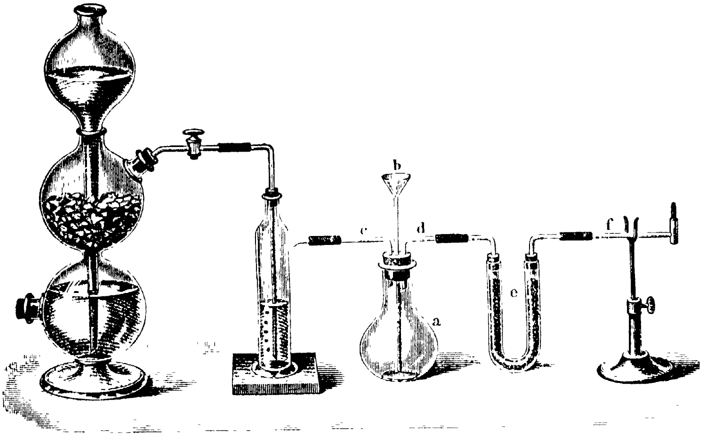

FIG. 57.

When the purity of the zinc and the sulphuric acid has been ascertained in this way, a few c.c. of dilute (1 : 5) sulphuric acid is poured into the flask through the funnel *b*. If phosphorus is present, the green coloration of the flame appears, although frequently not until after some time. In order to produce a hydrogen flame of sufficient size two Kipp's apparatus may be used, their outlet tubes being connected by means of a **T**-piece. The addition of a few drops of platinohydrochloric acid to accelerate the evolution of gas in these apparatus does not interfere with the reaction. In order to facilitate the observation of the flame with the naked eye, J. Dalmon [1] recommends holding a sufficiently long narrow tube, such as is used in the chemical harmonicon, and placing it in such a way that the flame is depressed against the inner wall of the tube. The flame thus becomes more compact without producing a musical note, and appears green over its whole area, while phosphorescent light waves are formed. If the tube is lowered the flame is compressed, and a dark blue coloration sometimes appears. It is doubtful, however, whether this is also due to the phosphorus; only the *green* coloration is decisive (G. Baumert).[1] By this method Nattermann and Hilger were able to detect 0·00006 mgrm. of phosphorus in the form of phosphite with the naked eye, whilst still smaller quantities may be detected with the spectroscope. The method is not suitable for a *quantitative* estimation, since only about a tenth to, at most, a fifth of the phosphorus present in the form of phosphite ion can be obtained as silver phosphide.

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[1] *Zeitsch. anal. Chem.*, **10,** 132 (1871).

The solution filtered from the silver precipitate (343) is freed from excess of silver by means of hydrochloric acid, filtered through filter paper which has been thoroughly washed with acid and water, the free hydrochloric acid expelled by repeated evaporation with nitric acid on the water bath, the residue dissolved in a little nitric acid, and the solution finally tested qualitatively for phosphate ion by means of molybdate reagent or a mixture of magnesium chloride, ammonium chloride, and ammonia. **345.**

According to R. Fresenius and C. Neubauer, the method is also very sensitive even in the presence of substances which prevent the luminescence of phosphorus in Mitscherlich's method. On the other hand, it has been almost as frequently asserted[2] as denied[3] that under certain conditions volatile substances containing phosphorus may be formed in putrefying organic matter and especially brain substance, and that these give the Dusart-Blondlot reaction (G. Baumert). Hence this test is not so conclusive as the occurrence of phosphorescence in Mitscherlich's method.

(c) *By expelling the phosphorus in a current of hydrogen.*

346. Since, according to Blondlot, treatment of the substance to be tested for phosphorus with zinc and sulphuric acid renders more difficult the further examination of the zinc-containing residue for other poisons, Dalmon[4] conducts pure hydrogen through organic substances containing phosphorus; the gas, under these conditions, taking up phosphorus. The ignited hydrogen flame is tested as described above (p.778) by placing over it a glass tube in the manner of the chemical harmonicon. On washing the tube, in which the hydrogen charged with phosphorus was burned, with a little water, the phosphate ion formed may be detected in the liquid by means of molybdate reagent. Neubauer,[1] who confirms Dalmon's statements, also calls attention to the fact that the escaping hydrogen charged with phosphorus shows a fine phosphorescence in a dark room.

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[1] *Lehrbuch der gerichtlichen Chemie*, vol. I, 2nd ed., p. 212 (1907).

[2] Selmi, *Ber.*, **9**, 1127 (1876); **11**, 1691 (1878); J. von d. Hagen and P. Woltering, *Chem. Zentr.*, 1893, II., 1103; C. Stich, *Zeitsch. Unters. Nahr. Genuss.*, **3**, 685 (1900).

[3] Z. Halász, *Zeitsch. anorg. Chem.*, **26**, 438 (1901); A. Fischer, *Pflüger's Arch. d. Physiologie*, **97**, 578 (1903).

[4] *J. chim. médicale*, 1870 .123; *Zeitsch. anal. Chem.*, **10**, 132 (1871)

(*d*) *By distillation with alcohol.*

347. If the substance to be examined is immersed in alcohol when received, the following method, devised by H. Hager,[2] may be recommended. The alcohol is removed by distillation on the water bath, after the addition of a little sulphuric acid, and of ferrous chloride if there is reason for concluding that phosphorus derived from phosphorus matches is present. No phosphorescence will occur in this process, but the distillate will consist of alcohol containing phosphorus. On repeating the distillation with fresh portions of alcohol, it is possible to separate small quantities of phosphorus *completely* in the distillate. On then filling a test-tube to a third of its capacity with water, pouring into it about 10 drops of the alcohol charged with phosphorus, and especially the fraction which distilled first, and shaking it in the dark, the whole tube will appear to be filled with phosphorescent light. The alcohol containing the phosphorus becomes brown or black on the addition of silver nitrate or copper sulphate solution, with separation of the respective metal phosphides and elementary metals, and formation of phosphate ion. A test with lead paper will readily determine whether any hydrogen sulphide present was the cause of the formation of the dark precipitate.

(*e*) *By extraction by shaking with solvents immiscible with water.*

348. On shaking liquid solvents for phosphorus, which are immiscible with water, with aqueous suspensions of organic substances containing free phosphorus, the latter is taken up by the solvents, and is left as a residue when they are carefully evaporated. For this purpose it is advisable to add a little water in order to protect the phosphorus from the oxidising action of the air, after evaporation of the solvent. Solvents proposed as suitable for this purpose include carbon bisulphide (Selmi,[1]), ether (Lassaigne [2] and van Bastelaer [3]), and petroleum spirit (H. Hager).[4] If the solvents are nearly removed by spontaneous evaporation at the ordinary temperature, the residues, when poured on to a flat dish in the dark, will, as a rule, immediately appear phosphorescent. They may then be submitted to further tests by the methods described above. In order to obtain the phosphorus in as pure condition as possible when mixtures containing fat are extracted with ether, van Bastelaer recommends that the residue, left on evaporating the ether in the presence of a little water, should be heated to 50° to 60°, that the resulting melted mass containing the phosphorus should be repeatedly shaken with concentrated ammonia solution to remove the fat, and that the phosphorus, which will not be appreciably attacked in the process, should then be washed, first with water containing a little sulphuric acid, and then with pure water.

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[1] *Zeitsch. anal. Chem.*, **10**, 132 (1871).
[2] *Pharm. Zentralh.*, 1870, 455; *Zeitsch. anal. Chem.*, **10**, 256 (1871).

B. Detection of Phosphite Ion.

349 If phosphorus in the free form has not been detected, tests must be made to determine whether the first product of its oxidation in the air, *phosphite ion*, may not be present. For this purpose the residue of the distillation in (338) or in (342) or (343) is introduced into the apparatus shown in Fig. 57 (p. 778), which has been charged and tested as in (344), and a note made whether the presence of phosphorus is indicated by the flame coloration of the ignited hydrogen (Wöhler). If such coloration appears, the aim of the test is attained ; if not, the presence of organic substances may be the cause of its non-occurrence. Should the flame not be coloured, the tube with a platinum point *f* is replaced by a U-tube containing a neutral solution of silver nitrate, the tap again opened, and the gas allowed to pass for several hours in a slow current through the silver solution. If phosphite ion was present, a precipitate containing silver phosphide will separate in the silver solution, and may then be further examined as in (344).[5] In this way T. Poleck [6] succeeded in detecting phosphite ion in a dead body three months after death, whereas free phosphorus could no longer be detected therein.

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[1] *Ber.*, **5**, 289.

[2] *Pharm. Zentralh.*, 1850, 360.

[3] *Zeitsch. anal. Chem.*, **13**, 350.

[4] *Ibid.*, **20**, 321.

[5] The statement of W. Herapath (*Pharm. J. and Trans.*, 1865, **7**, 573) that phosphoric acid is also reduced by zinc and dilute sulphuric acid is absolutely incorrect. *Cf.* the communications of R. Fresenius on this point (*Zeitsch. anal. Chem.*, **6**, 203).

[6] *Zeitsch. anal. Chem.*, **30**, 528.

4. Examination of the Inorganic Constituents of Plants, Animals, or portions thereof, Manures, etc. (Ash Analysis).

SEC. 208.

A. *Preparation of the Ash.*

350. For the purpose of a qualitative analysis, it is usually sufficient to incinerate a small portion of the substance to be examined for inorganic constituents, after careful purification. This is best done in a small earthenware muffle, into which the substance is introduced in a small porcelain or platinum crucible, although an obliquely-inclined crucible also answers the purpose well, and under certain conditions the ignition may also be effected in a small porcelain or platinum basin, a wide glass tube (cylindrical lamp glass) being used to promote the current of air. The heat must always be kept moderate to prevent volatilisation of individual constituents, especially chlorides. It is not always necessary to continue the ignition so far as to consume all the carbon. In the case of ash which contains much fusible salt, *e.g.* that of beetroot molasses, it is much better only to carbonise the mass by the application of moderate but long-continued heat, to boil the mass with water, and to complete the incineration of the washed and dried residue. The aqueous extract obtained must obviously be added again to the ash of the insoluble portion, or evaporated to dryness therewith. Full details of the most suitable method of incineration will be found in R. Fresenius' *Anleitung zur quantitativen Analyse.*

B. *Examination of the Ash.*

351. As in the case of waters of natural occurrence, no essential differences will be shown by the qualitative analysis of the ash of vegetable or animal substances, since the inorganic constituents which are present in any considerable proportion are the same in every case.[1] Leaving out of the question certain substances which in many cases are only present in small proportion and are absent in others, only a quantitative analysis can be regarded as sufficient to characterise an ash, and, as a rule, it may be made without a preliminary qualitative analysis, since the substances to which attention must be given are known.[1] A qualitative analysis of ash may always be of value, however, if it is made in such a way as to allow of an approximate estimation of the relative proportions of the different substances. To differentiate between ashes, it is particularly important to determine which substances (and what quantities thereof) are soluble in water and which are soluble and insoluble in hydrochloric acid. The following method of examination is suitable for this purpose :—

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[1] For this reason the analysis of ashes must be dealt with in detail in quantitative analysis. In this connection reference may be made to R. Fresenius' *Anleitung zur quantitativen Analyse.*

(*a*) *Examination of portions soluble in water.*

The ash is boiled with water, the liquid filtered, and the filtrate examined as follows, while the residue is being washed. **352.**

1. A portion is heated, treated with hydrochloric acid in excess, again heated and allowed to stand. Effervescence indicates the presence of *alkali carbonates ;* an odour of hydrogen sulphide indicates the presence of a sulphide of an alkali metal formed from a sulphate by the reducing action of the carbon. A turbidity, due to the separation of sulphur, and an odour of sulphur dioxide point to the presence of *thiosulphate* (occasionally found in coal ash). The liquid is filtered, if necessary, and treated with barium chloride. A white precipitate indicates *sulphate ion.*

2. A portion of the liquid is evaporated to a small volume, and rendered just acid with hydrochloric acid (effervescence indicates *carbonate ion*), a few drops tested for *borate ion* by means of turmeric paper (Sec. 109, 5), the main solution then evaporated to dryness, and the residue taken up with hydrochloric acid and water. A residue indicates *silicic acid.* It is filtered off, and a portion of it repeatedly evaporated nearly to dryness in a porcelain basin with nitric acid, and tested for *phosphate ion* by means of ammonium molybdate solution (Sec. 107, 10). **353.**

3. A portion is treated with silver nitrate solution as long as a precipitate forms, then gently heated, and ammonia solution cautiously added. If a black residue is left, it is silver sulphide (derived from an alkali sulphide or thiosulphate). The ammoniacal solution, **354.**

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[1] If, under exceptional circumstances, the analysis should be extended to include metals which are reducible on charcoal and volatilise at the temperature of ignition (*e.g.* arsenic, zinc, cadmium, lead), but which can only be found in plants or animals under very definite conditions, the substance under examination, instead of being incinerated, should be treated with hydrochloric acid and potassium chlorate (301), or by one of the other methods for the destruction of organic substances described in (284).

filtered if necessary, is treated with nitric acid in slight excess, so that the silver phosphate first formed is re-dissolved, and only silver *chloride* (iodide or bromide) is left. The precipitate is filtered off and the filtrate, carefully rendered exactly neutral with ammonia. If a pale yellow precipitate is formed, the phosphate ion formed in (353) is present in the ash as *ortho*phosphate, whilst if the precipitate is white it is present as *pyro*phosphate.[1] Portions of the aqueous solution of the ash are tested for iodine and bromine ions, and eventually for chlorine ion as in (178) and (180).[2]

355. 4. A portion is heated with hydrochloric acid, rendered alkaline again with ammonia, treated with ammonium oxalate, and allowed to stand. A white precipitate indicates *calcium*. The liquid is filtered, and the filtrate treated with ammonia and sodium ammonium hydrogen phosphate; a crystalline precipitate, which is often only perceptible after the liquid has stood for some time, indicates *magnesium*. (Magnesium ion often occurs in the aqueous solution in distinctly appreciable quantities, and calcium ion only in very minute traces, even when carbonates and phosphates of the alkali metals are present.)

5. Tests for *potassium* and *sodium* are made as in Sec. 173, and also, according to whether magnesium is present or not, as in (168) or (169) and (170).

6. *Lithium*, which is present in ashes much more frequently than was formerly believed to be the case, and *rubidium*, which almost invariably accompanies potassium, are most easily detected by means of spectroscopic analysis (Sec. 22) in the residue consisting of alkali salts.

(*b*) *Examination of the portion insoluble in water.*

356. 1. The greater portion of the ash which has been exhausted with water is heated (after further incineration if it contains much carbon) with hydrochloric acid (effervescence in this process indicating *carbonate ion* in combination with alkaline earth metals, and evolution of chlorine, *manganese oxides*). The whole is then evaporated to dryness after the addition of a few drops of dilute sulphuric acid, and the residue heated somewhat more strongly on an asbestos plate or sand bath to separate *silicic acid,* the residue moistened with hydrochloric acid containing a little nitric acid, and the liquid heated, diluted with water, and filtered from the insoluble residue. The latter is washed with water, and the filtrate and residue then tested as follows :—

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[1] Pyrophosphate ion can only be found in such ashes as contain no carbonate, or at most very small quantities thereof.

[2] To test with certainty for halogen ions in animal or vegetable substances, separate portions must be carbonised after the addition of sodium carbonate and the aqueous extracts of the resulting residues examined (*cf.* R. Fresenius' *Anleitung zur quantitativen Analyse*, II.).

(*a*) *Solution.* **357.**

(*aa*) A portion of the liquid is tested with hydrogen sulphide. If any precipitate, other than a pure white one, is produced, it may be examined by the ordinary analytical methods. (Plant ashes sometimes contain *copper*, and, under some conditions, also *lead.*)

(*bb*) A portion of the solution is treated with ammonia solution until the resulting precipitate no longer disappears when stirred, and ammonium acetate and a little free acetic acid then added, so as to render the reaction decidedly acid. In most cases this produces a white precipitate of *ferric phosphate*, which, under certain conditions, may be mixed with a little *aluminium phosphate.* It is filtered off, washed, and heated with pure hydroxide solution, the liquid filtered, and the filtrate tested for *aluminium ion* by acidifying it with hydrochloric acid and heating it with ammonia. If necessary, the residue insoluble in potassium hydroxide solution may be dissolved in hydrochloric acid, and the solution tested for *ferric ion* by means of potassium thiocyanate. If the liquid filtered from the precipitate (which consists solely, or in the main, of ferric phosphate) is reddish, more ferric ion is present than corresponds to the phosphate ion; if it is colourless, ferric chloride solution is added drop by drop until the liquid appears red. From the amount of precipitated ferric phosphate an estimate may be formed of the quantity of *phosphate ion* present. The liquid, which was originally reddish, or has been made so by the addition of ferric chloride, is heated to boiling point (if this does not render it colourless a little more ammonium acetate must be added, and the boiling repeated) and filtered while hot, and the filtrate neutralised with ammonia (any material excess being avoided) and again filtered, if necessary. The filtrate is treated with yellow ammonium sulphide in a boiling flask, which it nearly fills, the flask then closed and allowed to stand for some time, and the resulting precipitate filtered off, and tested as in (143) *et seq.* for *manganese* and *zinc*, which latter is exceptionally present in ashes. The liquid which has not given a precipitate with ammonium sulphide, or the filtrate from a precipitate produced by that reagent, is tested for *calcium* (with which a little *strontium* may be mixed) and for *magnesium* as in Secs. 171 and 172.

(β) *Residue.*

358. The residue insoluble in hydrochloric acid contains the silicon dioxide separated by the treatment with hydrochloric acid, any barium present, the greater portion of any strontium present, and possibly some lead, in the form of sulphates, and lastly the original insoluble constituents of the ash itself. In the case of most ashes these consist of sand, clay, and charcoal, *i.e.* of substances due to the imperfect purification or combustion of plants, etc., or derived from the crucible. Only in the case of the very silicious ashes of cereal haulms, etc., is a portion of the real ash not completely decomposed by hydrochloric acid.

The washed residue is boiled for some time with a solution of sodium carbonate, the liquid filtered while hot, the residue washed with boiling water, and *silicic acid* detected in the filtrate by evaporating the latter with hydrochloric acid as in Sec. 115, 3. The insoluble portion of the residue is heated with very dilute nitric acid, and the resulting solution tested for *lead*, *barium*, and *strontium ions* by the ordinary methods.

If the ash was completely decomposed by hydrochloric acid, this part of the examination may usually be regarded as complete (for it is seldom a matter of interest to make a further examination of adventitious admixtures of clay and sand by fusion methods); but if the ash was rich in silicic acid (a fact suggesting that it was not completely decomposed by hydrochloric acid), half of the insoluble matter left when the residue was boiled with sodium carbonate solution, and then extracted with nitric acid and washed, is evaporated to dryness with excess of pure sodium hydroxide solution in a silver or platinum basin. By this treatment the silicates of the ash are decomposed, whereas any sand present is but little attacked. The new residue is acidified with hydrochloric acid, the liquid evaporated to dryness, and tests applied as in (356). For the detection of alkali metal ions in the portion of the ash insoluble in water, the other half of the above-mentioned washed residue is examined as in (228). If alkali metal ions are found here, however, they can only be regarded as part of the real ash, if the latter was free from clay and other impurities which might possibly contain alkalis.

2. The remainder of the ash which has been extracted with water **359.** may be tested for *fluorine ion* as in Sec. 111, 7, but since, during the incineration, substances containing fluorine are lost (Tammann[1]), and the residual portion may, under certain conditions, be partly dissolved by water, it is essential, when a definite decision is required as to whether an animal or vegetable substance contains fluorine, to heat a separate portion of the substance with pure potassium or sodium hydroxide solution, to evaporate the mixture to dryness, and to incinerate the residue. The residual ash is then tested as in Sec. 111, 8.

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[1] *Zeitsch anal. Chem.*, 24, 342.

CHAPTER III.

EXPLANATORY NOTES AND ADDITIONS TO THE PRACTICAL PROCESS.

I. Notes on the Preliminary Examination.

From Secs. 150 *to* 152 *inclusive.*

1.[1] It is frequently possible, as mentioned above in (1), from a consideration of the physical properties of a substance, especially when it is not a mixture, to draw a definite conclusion as to its general nature. If, for example, a substance is white, the inference may be drawn that it is not cinnabar; if it is light, the presumption is that it is not a lead compound, and so on.

Such inferences frequently lead more rapidly to the end in view, and are therefore more trustworthy and advisable, so long as they are confined to generalities. When, however, they exceed this limitation, they easily become guesswork, for preconceived opinions are formed which almost invariably lead to inaccurate results, owing to their tendency to make the observer blind to the occurrence of reactions which point in the opposite direction.

2. In order to test the behaviour of a substance at high temperatures, a small spoon of iron or platinum foil, a crucible lid, or a small porcelain basin may be used, instead of a sealed glass tube (3), but the results obtained in a tube can usually be observed more readily, whilst the nature of any volatile substances can be ascertained more easily, and there is less chance of their escaping detection. Sometimes it is advantageous to heat a portion of the substance in a short glass tube open at each end, and slightly constricted at the bottom, the tube being held in a slanting position, or to heat it in a glass tube bent at an obtuse angle (*i.e.* in a current of air), so as to gain information concerning any oxidation products which may be formed. Small quantities of a metal sulphide, for example, may thus be readily detected (Sec. 124, 8). Arsenic and antimony compounds yield sublimates of the oxides (sometimes in the case of arsenic mixed with elementary arsenic, and always accompanied by an odour of garlic).

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[1] These rubric numbers are used in the same way as in the systematic course to facilitate the cross references; in all references they are prefixed by "No."

The method of determining the behaviour of the substance when heated depends upon the circumstances. If there is a possibility of an explosive substance being present, it is advisable to heat only a small amount upon a crucible lid, or the like. If the odour of the escaping vapour is to be observed, it is often preferable to use a basin or crucible lid rather than a glass tube, whereas the formation of a sublimate may be seen better in a tube. If a substance, when heated in a glass tube, yields vapour (8) or a sublimate (9), care must be taken, in noting the odour of the vapour there formed or produced when the substance is heated on charcoal (11), not to inhale any considerable quantity of the injurious vapours of mercuric salts or other volatile poisonous substances.

If the preliminary examination shows that organic substances **3.** (possibly mixed with inorganic substances) are present (8, *kk*), (10), (26), it is necessary in many cases to make use of other methods, not corresponding with the ordinary conception of qualitative analysis for their qualitative examination. For the identification of such substances, the methods of organic chemistry must be utilised—methods which in many cases are based upon a determination of physical constants (melting-point, boiling-point, etc.), or also of chemical constants (percentage, composition as estimated by elementary analysis, or molecular weight, saponification value, etc.), which cannot be dealt with here.

In view of the large number of compounds, the task of ascertaining the nature of any given organic substances appears extraordinarily difficult. In the majority of cases, however, conclusions may be drawn from other circumstances, such as the origin, use, etc., as to the kind of substances which might possibly be present, so that then the number of substances for which tests must be applied is materially reduced. In this book only the organic acids of more frequent occurrence (and the more important alkaloids) are dealt with. Hence, it is only for the detection of these that the systematic course described is applicable.

With regard to the blowpipe tests (11) to (17) especially, **4.** beginners must be warned not to infer *too much* from the results, for it requires considerable practice to produce the phenomena with certainty, and some experience is indispensable for their correct interpretation. In particular we may call attention to the fact that illuminating gas only gives a luminous true reducing flame when it is sufficiently rich in hydrocarbons (does not contain too much water gas). If this is not the case, the defect may be remedied by the introduction of carbon into the gas (p. 76).

5. Lastly, as a matter of experience, it may be mentioned that many beginners, with the idea of saving time and trouble, attempt to ascertain the nature of a substance by means of the actual examination, while entirely omitting the preliminary examination. Instead of demonstrating the unwisdom of this view, it need only be mentioned by way of illustration that those obsessed by such an idea may be seen spending hours in searching for all the organic acids, only to discover at last that none of them is present. And all this trouble is taken merely to save time and trouble! Especially, however, should the attention of beginners be directed to the increase of knowledge which will result from practice, observation, and drawing conclusions directly from the preliminary examination, and by which it will be seen that the results here obtained, although often only of general applicability, must never be contradictory to the specific results of the actual examination.

II. Notes on the Solution of Substances, etc.

Secs. 153 *to* 156 *inclusive.*

6. If we consider the characteristics of the classes given in (31), into which substances, with the exception of elementary metals, may be grouped in accordance with their behaviour towards solvents, the classification appears to be more sharply defined than is really the case. This indefiniteness is due to the sparingly soluble substances occupying a position on the boundary line, and frequently causes the beginner to draw erroneous conclusions. Hence some further details of this general classification must be given.

The most difficult question is to determine exactly which substances are to be regarded as soluble and which as insoluble in water, since a very large number of substances are only very slightly soluble in water, whilst *absolutely* insoluble substances do not exist, and the transitions are gradual. Calcium sulphate (soluble in about 450 parts of water) might, perhaps, be adopted as the limit, since it can be identified with great certainty in aqueous solution by means of the sharp reagents for calcium and sulphate ions at our disposal.

When an aqueous liquid is evaporated to a small volume to ascertain whether it contains a solid substance in solution, a very trifling residue is often left, and the conclusion to be drawn from it is doubtful.[1] In such cases the reaction of the liquid is first determined by means of litmus paper, then a portion is tested with a drop of barium chloride solution, and finally a little sodium carbonate solution is added to a second portion. If these reagents cause no change, and the liquid is also neutral, it is, as a rule, unnecessary to apply any further tests. The conclusion may be drawn that the substance from which the slight permanent residue left on evaporation was derived may be more readily identified in the substances insoluble in water, since both the cations and anions which principally form sparingly soluble compounds may be detected by the sensitive reagents used.

If, in the examination of mixed substances not completely soluble in water, something has dissolved, it is best to apply separate tests for the cations and anions to the aqueous solution, since by such means the nature of the compounds present may be more easily ascertained and with greater certainty—two advantages which outweigh the drawback of having to test for the same substance in both aqueous and acid solutions.

Substances practically insoluble in water but soluble in hydrochloric or nitric acid include, although with exceptions, phosphates, arsenates, arsenites, borates, carbonates, and oxalates (except those of the alkali metals), also various tartrates, citrates, malates, benzoates, salicylates, and succinates, oxides and sulphides of heavy metals, oxides of aluminium and magnesium, many iodides and cyanides, etc. Although nearly all of these compounds are decomposed by concentrated hot hydrochloric acid, if not by dilute acid (for exceptions, see Sec. 179), yet, in the presence of silver, mercurous, or lead ions, insoluble or nearly insoluble compounds are formed in the process. This is not the case when nitric acid is used, so that complete solution may often be effected by means of that acid when hydrochloric acid leaves a residue. On the other hand, nitric acid does not dissolve antimony oxides, tin oxides, manganese dioxide, lead peroxide, etc. (in addition to the substances insoluble in simple acids in general), and dissolves many others (*e.g.* ferric oxide and aluminium oxide) less readily than hydrochloric acid.

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[1] If the test is made by evaporating the liquid on the cover of a platinum crucible over a free flame, fusible substances, such as alkali salts, may easily be overlooked until they are observed exactly at the moment of solidification or fusion when cooled or heated again. Colourless substances evaporated in porcelain dishes may also easily be missed when they are only present in small proportion, and the test is made over a free flame. Evaporations on a clock-glass can only be carried out on the water bath or on an asbestos plate.

Briefly stated, the method of treating substances insoluble in water is, therefore, as follows: An attempt is made to dissolve them in dilute or concentrated hot or cold hydrochloric acid; if no solution or only partial solution takes place, another portion of the substance is treated with nitric acid; if this is also unsuccessful, the substance is treated with *aqua regia*, which is a particularly suitable solvent for metal sulphides. A separate examination of a hydrochloric or nitric acid solution, or of a solution in *aqua regia*, is, in most cases, neither necessary nor desirable. The preparation of an *aqua regia* solution, when the nature of the substance does not make it essential, is also undesirable, since a hydrochloric acid solution is much more suitable for hydrogen sulphide precipitations. Hence, in many cases, when the substance does not dissolve completely in acid, the preparation of an *aqua regia* solution may be avoided, and it is usually possible to prepare a hydrochloric acid solution, and to examine the residue as in Sec. 179. Some experience is required to decide whether this is practicable, and absolutely definite rules cannot be given here. An indication is obtained by washing the substance which has been exhausted with hydrochloric acid, treating it with *aqua regia*, and evaporating the liquid separated from the insoluble residue to see whether anything further has been dissolved.

If this test is to be used, it is advisable in the examination according to (40) not to use the whole of the substance which has been treated with concentrated hydrochloric acid, but to filter off and wash a portion thereof. In concentrating an *aqua regia* solution by evaporation, to remove the excess of acids, it must be borne in mind that volatile chlorides (*e.g.* mercuric chloride) may be volatilised, at all events partially, at the same time. Hence, the amount of acid mixture used for preparing the solution should only be just sufficient for the purpose.

Solutions obtained by means of hydrochloric acid usually contain metals in the state of valency in which they were originally present (peroxides and oxides closely related to them form exceptions, as do also mercurous compounds, since mercurous chloride, when boiled for a long time with hydrochloric acid, is gradually decomposed into mercury and mercuric chlorides). If, however, solutions are prepared by means of nitric acid or *aqua regia*, oxidations frequently take place, divalent iron, for example, is converted into the trivalent condition, divalent into tetravalent tin, and trivalent into pentavalent arsenic ; this must always be borne in mind.

If colloidal silicic acid separates in the course of the treatment with acids (33, *c*) (38), it is necessary to decide from the conditions whether merely the presence of natural silicates is indicated, in which case the process described in Sec. 182 is followed, or whether, in addition to the constituents which experience has shown only to occur in such minerals, there may not also be present other substances (*e.g.* in the case of artificial glass fluxes, enamels or the like, or of mixtures of silicates with other substances). In this case the examination of the solution and of the residue must not be restricted to the substances mentioned in Secs. 181 to 184, but the comprehensive course given in Sec. 164 *et seq.* and in Sec. 179 must be followed. **7.**

In connection with the solution of elementary metals and alloys (43), it should be noted that when these are boiled with nitric acid they sometimes yield white precipitates, even when the metals mentioned in (44), *i.e.* tin or antimony, or even silicates, are not present. These precipitates are often mistaken by beginners for oxides of the elements mentioned, although they have quite a different appearance. They are salts of nitric acid, which are only sparingly soluble in the nitric acid present, but are readily soluble in water. Before concluding that an insoluble white residue is due to tin, antimony, etc , it is advisable to see whether it does not dissolve in water. **8.**

III. Notes on the Actual Examination.

Attention must be directed here to many points which, in order not to interfere with the general survey, could not be dealt with, or only briefly touched upon, in the course of the analysis. It will also be shown briefly, and in small type, how the analytical scheme is extended when elements or compounds of rarer occurrence have to be taken into consideration in an examination.

General notes on the course of analysis for simple compounds.

Secs. 157 *to* 163.

As was pointed out on p. 546, the course of analysis for " simple compounds " is really only an instructional course, since there is no external criterion by which a simple compound may be recognised definitely *as such*, and hence in the examination of really unknown **9.**

substances there can obviously never be any certainty that *only* one cation and one anion is present. It is, however, very suitable as an introduction to systematic analysis, because it sets before beginners at the outset only a limited task, the execution of which and the deductions to be drawn from the results can be more readily grasped.

As the object of the course for simple compounds is instruction, only the ordinary conditions are taken into consideration, and particularly complicated cases are not brought to the notice of the beginner, in order not to confuse him.

As a rule, the salts are to be regarded as neutral, although obviously an oxide or a free acid may be presented for examination.

At first it is advisable only to set the task of detecting the cation in an aqueous solution (*cf.* Appendix II.). When a knowledge of the methods used for this purpose has been acquired, the examination of simple compounds in solid form may then be undertaken.

The aim of these analytical examinations is not to discover as rapidly as possible what substance is present, but to gain practice in observation and in drawing correct conclusions, to become really acquainted with the course and thoroughly familiar with the properties of the substances to be examined—their appearance, behaviour, and solubility. Hence, the preliminary examination and the determination of the behaviour of the substance towards solvents is now associated with the actual examination, and the conclusions drawn from the former, which are sometimes only of a general character, are compared with the results obtained in the actual examination.

In particular, attention may be drawn to the use of the solubility Table I. (Appendix IV.), in deciding which anion may be combined with the cation found (Secs. 158, 159, 161, 162, in each case at the beginning or in the preceding general survey), and also because the use of this table impresses upon the mind the solubility proportions of the actual salts, which are not really investigated.

10. The condition that only *one* cation and *one* anion shall be present is only really fulfilled in the case of *absolutely pure* substances. In practice, it is frequently impossible to avoid having the material under examination contaminated with very minute quantities of impurities.

In such cases, the use of the different reagents may, under certain conditions, produce *slight* precipitates (*i.e.* faint reactions), which are not due to the actual substance under examination, or do not indicate its presence. These may be ignored. After a little practice it will be found easy to distinguish such faint reactions from those which are really significant. A quite general indication is afforded by the fact that when a solid substance has originally been dissolved, the amount of any precipitate formed must be approximately as much as the amount of substance contained in the quantity of solution taken.

General notes on the analytical course for mixed compounds.

Secs. 164 *to* 179.

An analytical course for mixed compounds should be applicable **11.** to all conceivable cases. If, however, attention had always to be directed towards every possible substance, the course would become so overloaded with details, which in most cases would be of no importance, that it would lose in clearness of outline, and would become much more circumstantial and tedious than is necessary for ordinary purposes.

Hence, in Chapter II. the elements and compounds of rarer occurrence are not included (although they are dealt with in *these* notes); further, in the examination for cations, for example, the case is taken into consideration of all the anions simultaneously present not being particularly noticeable, whilst allowance is also made for the difficulties caused by the anions in certain cases. In like manner, both in the case of the cations and of the inorganic anions, the more simple case is presented in which organic substances are not present, whilst at the same time directions are given as to the special precautions which are necessary when they are present. This method of treatment not only enables the abbreviated course to be used in practice under simpler conditions, but also makes the student familiar from the first with a scheme of analysis which he can more easily grasp as a whole.

The process for the detection of different substances in the **12.** presence of each other in the same solution is based in the examination for cations upon the complete separation of all the members belonging to a group in the form of a precipitate, so that the filtrate is free from them, and upon the removal of the substances still in solution, by washing the precipitate to remove the last adhering portions of the filtrate. It is, therefore, a primary essential that both the precipitation and the washing should be complete, and it is consequently necessary to prove that this condition has been complied with, on the one hand, by adding a small amount of the precipitant to the filtrate, and, on the other hand, by testing the washing water (see p. 42).

If this is not the case, the conclusions drawn from the subsequent examination of the different precipitates will often be uncertain or entirely false, because they are only justified on the assumption that a precipitate no longer contains any substances which cannot be precipitated by the reagent used to produce it, or that a solution is free from substances precipitable by the precipitating reagent previously used. If, for example, a solution contains lead and iron ions in addition to Group VI., it will yield a black precipitate with hydrogen sulphide. If this precipitate is not thoroughly washed, prior to treatment with ammonium sulphide, the iron ion will also be precipitated from the adherent solution, and, on treating the nitric acid solution of the residue with ammonia at the point where bismuth ion is to be precipitated, a yellowish-brown precipitate of ferric oxide will be obtained instead of a white precipitate, and will mask any precipitate of bismuth hydroxide present, or at all events interfere with conclusions. Or, if a solution which contains barium ion in the presence of cupric ion is treated with hydrogen sulphide, and the precipitate is not thoroughly washed, a precipitate of barium sulphate will be obtained on subsequently testing the nitric acid solution with sulphuric acid, and may be mistaken for precipitated lead ion. Or, again, if lead and zinc ions are simultaneously present in a solution, and if (*e.g.* owing to acidity being too high) the lead ion is not completely precipitated with hydrogen sulphide, the addition of ammonium sulphide to the filtrate will produce a black precipitate, which is only partly soluble in dilute hydrochloric acid, and the insoluble portion of which might be taken for cobalt or nickel sulphide (although the fact that the solution was colourless is opposed to such conclusion).

13. In making analyses of mixed compounds, it is in practice necessary, after the *main essentials* of the process have been grasped, to accustom one's self to make several examinations at the same time. Thus, when a precipitate has been obtained with a group reagent (*e.g.* hydrogen sulphide), a further test may be made immediately after the filtration of the first portion, to determine whether a precipitate is produced in the filtrate by ammonium sulphide, and, if not, by ammonium carbonate. After filtration of a solution, the next precipitate may be produced in the filtrate at once, without waiting until the first precipitate is completely washed. In like manner, two or three such group precipitates may be simultaneously subjected to further treatment. It is essential for this treatment, however, that the general grasp of the whole examination should not be lost, and that some method of recording the observations should be adopted, in which, as soon as an operation is finished, the results obtained may be entered in the appropriate place (see Appendix III.).

Special Notes and Additions

To Sec. 157 (46–49) *and Sec.* 164.

Directions were given at the beginning of Secs. 157 and 164 to treat neutral or acid aqueous solutions with hydrochloric acid. It is best to do this drop by drop. If no precipitate is formed, a small addition is usually sufficient, because at that stage the liquid is only acidified to prevent the precipitation of metals of the fourth group by hydrogen sulphide. If a precipitate is formed, a new portion might be taken and acidified with nitric acid, as has been recommended by others But, apart from the fact that in many cases this will also produce a precipitate, *e.g.* in a solution of potassium antimonyl tartrate (tartar emetic), we prefer the use of hydrochloric acid, *i.e.* the complete precipitation of substances precipitable thereby, for three reasons Firstly, metal ions are more readily precipitated from a solution acidified with hydrochloric acid than from one acidified with nitric acid ; secondly, the subsequent analysis is materially facilitated when silver, mercurous, or lead ions are in solution, by the complete or partial precipitation of those metals as chlorides ; and thirdly, it is not possible to separate these three cations in a form more suitable for identifying them in the presence of each other than that of chlorides. Moreover, the use of hydrochloric acid obviates the necessity for further tests as to whether any mercury ion detected among the metals of the fifth group was present as mercurous or mercuric ion. The fact that lead ion, if present in considerable quantity, will be found both among the chlorides and in the precipitate produced by hydrogen sulphide in acid solution can hardly be cited as an objection to this method, since the examination for other members of the fifth, and also of the sixth group, will only be facilitated by the removal of most of the lead from the solution at the outset. **14.**

The precipitate of the two insoluble chlorides and of the sparingly soluble lead chloride produced in neutral or acid solutions (102) to (103) may also contain antimonyl chloride, $SbOCl$, (separated, *e.g.* from tartar emetic or an analogous compound), also bismuthyl **15.**

chloride, and, if the solution was concentrated, also barium chloride, metastannic chloride, and, silicic acid; and, if the solution contained any of the organic substances which have to be taken into consideration here, cinnamic, benzoic, or salicylic acid may also be present in the precipitate. Antimonyl chloride and bismuthyl chloride are re-dissolved on increasing the amount of hydrochloric acid. They have, therefore, no influence on the further examination. Barium chloride, metastannic chloride, benzoic acid, and salicylic acid are not precipitated from dilute solutions, and if the directions given are exactly followed, none of these substances will be present in a permanent precipitate. Silicon dioxide is gelatinous; in the exceptional cases where it is not precipitated by hydrochloric acid from an alkaline solution, the method given in (60) is used in the case of simple compounds, and that given in (106), footnote 2, in the case of mixed compounds. If organic substances are present, the precipitate is treated with ether. If it dissolves completely, mercurous, silver, and lead ions are not present. If it does not dissolve completely, the precipitate, thus freed with ether from organic substances, is tested as in (47), (103), or (106). It is neither necessary nor desirable to heat the liquid after the addition of excess of hydrochloric acid, since this might convert mercurous chloride, if precipitated in small amount, into mercuric chloride.

On washing the precipitate produced by hydrochloric acid, a turbidity or a precipitate may be formed when the washings are added to the first filtrate, if bismuthyl chloride, antimonyl chloride, lead chloride, or metastannic chloride is present, this occurring in the presence of bismuthyl or antimonyl chloride when the amount of hydrochloric acid present is not sufficient to prevent the separation of the basic salts which cause the turbidity; whilst in the presence of lead chloride or metastannic chloride, it takes place when the chlorides, which have been precipitated and re-dissolved by washing with water, encounter a sufficient quantity of hydrochloric acid in the filtrate to cause re-precipitation. Whether a precipitate is produced or not, the further course of the analysis is not altered; for these finely distributed precipitates are converted into sulphides as readily as though they were metal ions in solution.

The presence of barium chloride in the precipitate produced by hydrochloric acid may also, when removed by washing, cause a turbidity in the filtrate. But since this re-dissolves on further dilution with water, it does not interfere with the intelligent completion of the analysis.

If the precipitate which was treated with excess of hydrochloric acid and washed contained benzoic or salicylic acid, these acids would be dissolved in the subsequent treatment with hot water at the same time as lead chloride, but would not interfere with the detection of lead ion in this solution.

On adding hydrochloric acid to an *alkaline* solution, (104) to (108), **16.** care must be taken to continue the addition, drop by drop, until the liquid has a strong acid reaction. The substance causing the alkaline reaction is neutralised by the acid, and the substances kept in solution by, or combined with, it are precipitated. If alkali compounds of the nature of zincates or aluminates were present, these may also be precipitated here, *e.g.* zinc or aluminium hydroxide, etc. These, however, re-dissolve in excess of hydrochloric acid, whereas silver chloride or silicic acid is not re-dissolved, and lead chloride only with difficulty. If the alkaline reaction was due to a sulpho-salt containing a metal in its anion, the addition of hydrochloric acid will precipitate a metal sulphide (*e.g.* antimony sulphide), in some cases mixed with separated sulphur; whilst at the same time chlorine ion remains in solution, together with alkali (or ammonium) ion present, and hydrogen sulphide escapes; if it was due to a carbonate, cyanide, or sulphide of an alkali metal, carbon dioxide, hydrogen cyanide, or hydrogen sulphide will be liberated. All these phenomena must be duly observed, for they not only enable the presence of the substances in question to be recognised, but also exclude whole series of substances from the examination. Thus, for example, no cations, the carbonates of which are insoluble in water, can be present simultaneously with the carbonate of an alkali metal, etc.

Hydrochloric acid also produces precipitates in solutions which contain **17.** thallium compounds or alkali antimonates, tantalates, niobates, or tungstates.[1] Those due to antimonic, molybdic, and tantalic acid dissolve in excess of hydrochloric acid (the tantalic acid precipitate forming an opalescent solution), whereas thallous chloride, niobic acid, and tungstic acid are either insoluble or only sparingly soluble on adding such excess. Hence, these latter, if present, will remain behind in the precipitate, which may also contain silver, mercurous, and lead chlorides, as well as silicic acid. A separation of sulphur occurring some time after the addition of hydrochloric acid, would, if also accompanied by an odour of sulphur dioxide, indicate the presence of thiosulphate ion. If there is reason to infer that the precipitate produced by hydrochloric acid may contain elements of rarer occurrence, it should be boiled with water, and washed with boiling water, and the filtrate tested for thallium ion by means of potassium iodide. (Confirmation is obtained by means of the spectroscope.) On treating the precipitate, thus extracted with water, with ammonia solution, silver chloride is dissolved (either partly or completely), as is also any tungstic acid present. On then adding ammonium sulphide to the solution, silver sulphide is precipitated, whilst tungsten sulphide is precipitated by treating the filtrate from the silver sulphide with hydrochloric acid. Mercurous chloride is converted by this treatment into a black mixture of very finely divided mercury and mercuric ammonium chloride, which may also retain silver chloride (J. Barnes, Moeck) (*cf.* p. 284). When the residue is treated as there described, the metallic silver may be extracted by means of dilute nitric acid, silicon dioxide volatilised by means of hydrofluoric acid and sulphuric acid, and the residue of niobic acid left after the fusion with potassium hydrogen sulphate dissolved in dilute hydrofluoric acid.

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[1] Hydrochloric acid precipitates ordinary tungstic acid from solutions of salts of metatungstic acid, though only after boiling for some time.

Notes to Sec. 157 (50) *to* (55), *and to Secs.* 165 and 166:

18. The separation of the different groups of metal ions by means of hydrogen sulphide in acid solution and by means of ammonium sulphide depends upon the fact that the solubility product of metal sulphides decreases with the rise in the analytical groups, and that hydrogen sulphide is only slightly dissociated, whereas ammonium sulphide is dissociated to a considerable extent. The result is that in the case of Groups V. and VI. the concentration of the sulphide ions of the hydrogen sulphide is sufficient to cause the solubility product to be exceeded, whilst this is not the case with Groups I. to IV. The higher concentration of the sulphide ions when ammonium sulphide is used is then sufficient to cause the solubility product to be exceeded in the case of Group IV., but is not sufficient for that purpose in the case of the first three groups. But, since in accordance with the law of mass action, the dissociation of the hydrogen sulphide is checked by the hydrogen ions of acids simultaneously present, and since the more acid the solution of the metal salt the fewer will be the number of sulphide ions present, it follows that it depends upon the nature and quantity of the acid simultaneously present whether, and if so to what extent, hydrogen sulphide precipitates the metal ions of Groups V. and VI., whilst, on the other hand, when the hydrogen ion concentration is only slight, precipitation of sulphide in acid solution may occur in the case of certain members of Group IV. (zinc ion in very dilute sulphuric or acetic acid solution, and to some extent also iron ions in acetic acid solution). It is here to a considerable extent a question of reversible reactions in accordance with the general formula, $M^{\cdot\cdot}+H_2S\rightleftarrows MS+2H^{\cdot}$, the course of which in the direction from left to right may be influenced or entirely prevented by the presence of considerable amounts of hydrogen ions, and, on the other hand, requires the presence of an excess of hydrogen sulphide.

In other words, the precipitation of the metal ions of the fifth and sixth groups only takes place when the solution does not contain too much acid, and a sufficient quantity of hydrogen sulphide has been used. These conditions vary somewhat in the case of different metal ions. Thus, for example, there is interference with the precipitation at a lower acid concentration in the case of lead ion, and especially of cadmium ion, than in the case of the ions of the other metals. Hence, the separation of Group IV. from Group V. is not sharp under all conditions.

With regard to the practical application of the method, the following remarks may be made :—

1. Hydrogen sulphide must always be used in sufficient quantity ; thus when using hydrogen sulphide water, care must be taken that it is still in good condition, *i.e.* that the gas originally present in solution has not volatilised or been decomposed by keeping it too long or under unsuitable conditions ; the odour should be noted, and, if necessary, the action of the solution upon the solution of a metallic salt should be tested (*cf.* p. 73, footnote 5).

2. There should be a medium and, above all, not too high a concentration of hydrogen ions in the solution.

To satisfy these two requirements, it is well, when examining a solution to see whether it contains metal ions of Groups V. or VI., to add to a *small* portion of the solution, previously acidified, *several times its volume* of hydrogen sulphide water in good condition.

In testing the filtrate from a precipitate produced by hydrogen sulphide, the same procedure must be followed, *i.e.* a sufficient excess of hydrogen sulphide water must be added, and, if the precipitation is incomplete, the liquid is diluted before adding more of the reagent, for from what has been said it is clear that if the liquid is too acid the precipitation may be incomplete or may not take place at all.

The production of a precipitate by means of hydrogen sulphide **19.**
may also be influenced, checked, or prevented by the fact that the solution under examination has an oxidising action upon the hydrogen sulphide, in which process water or hydrochloric acid are usually formed, and the sulphur separates in elementary condition. There is an especial risk of this happening in the case of nitric acid

solutions (particularly those treated with hydrochloric acid) or of *aqua regia* solutions, both when they are strongly acid, and when they have been treated at too high a temperature. In this case, the sulphur often separates, not in a finely pulverulent condition, but in coherent masses (51, I., *b*) or (112). It may then mask or envelop any sulphide precipitate which has been formed, and render its subsequent treatment more difficult, even when eventually complete precipitation of the sulphide has occurred. Hence, so far as it is possible (*cf.* No. 6), it is advisable first to heat such solutions until they no longer smell of chlorine, then to *dilute* them, and to treat them in the cold with hydrogen sulphide.

20. The precipitation of pentavalent arsenic (arsenate ion) by means of hydrogen sulphide can only be effected by heating the solution to at least 70°. It is, therefore, sometimes advisable (especially when a nitric acid or *aqua regia* solution is present) to add, when practicable, an aqueous solution of sulphur dioxide, or another suitable reducing agent, to convert the arsenic beforehand into the trivalent condition, and so to obviate the drawbacks mentioned above (No. 19).

21. It is stated in (51) to (55), (112), (113), and (118) that conclusions may be drawn from the colours of the precipitates. To do this a certain amount of caution and experience is necessary. On the one hand, even in the case of simple compounds, traces of impurities may cause pale precipitates to appear darker, whilst, in the case of mercuric ion, an error may result from the fact that it is only when the separation is complete, *i.e.* when a sufficient excess of hydrogen sulphide has been added, that really black mercuric sulphide is precipitated ; or, again, a white precipitate of sulphur occurring in a yellow solution (*e.g.* containing ferric ion) may be regarded as a yellow precipitate. (In both the last two cases errors may be avoided by adding a sufficient quantity of hydrogen sulphide, and in the last case by heating the liquid.) On the other hand, small amounts of pale precipitates may be masked by the simultaneous separation of sulphur (for further details, see No. 27), whilst small quantities of dark precipitates may be masked by larger quantities of a yellow or orange precipitate. Lastly, under certain conditions, in the case of solutions containing ions of several metals, precipitates may be obtained, the colour of which is not a simple mixture of the colours of the individual sulphides. Thus, for example, a mixture of stannic chloride and mercuric chloride solutions may yield a fine yellow or orange-red precipitate.

In like manner, a solution of a lead salt in strong hydrochloric acid may give an orange-red precipitate of lead sulpho-chloride (which might be mistaken for antimony sulphide) instead of a black lead sulphide precipitate.

Moist sulphides, when exposed to the air, are partially oxidised to sulphates, which differ from sulphides in their characteristics as regards colour, solubility, etc *Hence, sulphide precipitates must not be allowed to remain exposed to the air in the moist condition*, because difficulties in the further manipulation may then be experienced. (Cupric sulphate, for example, may be dissolved during the washing, and be encountered in the fourth group, and nickel and cobalt sulphides do not remain insoluble during the treatment with hydrochloric acid.) **22.**

If, therefore, it is not possible to deal with a sulphide precipitate without delay after the filtration and washing, it is better to allow it to remain beneath the unfiltered liquid from which it was precipitated. If, however, it is necessary to reserve a precipitate which has been filtered off, the tube of the funnel should be closed by means of a piece of rubber tubing and a spring-clip (or a fragment of glass rod may be inserted in the tubing), and the precipitate then covered with hydrogen sulphide water or ammonium sulphide solution; or the precipitate may be transferred by means of a jet to a basin or beaker, and then covered with the reagent.

Since, even during the washing, there is some risk of oxidation, hydrogen sulphide water should be added to the washing water when the liquid passes only slowly through the filter, or when the precipitate was formed in an alkaline solution.

The separation of members of Group VI. from those of Group V. depends on the formation of sulpho-salts, soluble in water, during the treatment of the sulphides of the sixth group with ammonium or sodium sulphide. Such sulpho-salts are only readily formed by arsenic and antimony sulphides, and by stannic sulphide, whilst stannous sulphide does not form a sulpho-salt with alkali monosulphides. Hence a yellowish alkali sulphide (containing some polysulphide) must be used. Too large a proportion of polysulphide (recognisable by the dark yellow colour) must be avoided, however, since otherwise members of Group V (especially cupric sulphide) may also dissolve, but also, in particular, for the reason that so much sulphur separates from the filtrate from the insoluble sulphides of Group V. on treatment with hydrochloric acid, that, as a rule, it is not possible to observe the precipitation of coloured sulphides of the sixth group, which may also take place. **23.**

Gold and platinum sulphides are also not readily soluble with certainty in alkali sulphide solution. It is, therefore, necessary to anticipate the presence of certain proportions of tin, gold, and platinum among the members of the fifth group.

24. Since, as has been mentioned, cupric sulphide is not insoluble in ammonium sulphide solution, especially when the latter contains polysulphide, it is better to use sodium sulphide for the separation of the fifth from the sixth group in the presence of cupric sulphide. This can only be done, however, when no mercuric sulphide is present in the sulphide precipitate, since the former dissolves to an appreciable extent in sodium sulphide solution, and this would interfere with the examination for members of Group VI. Hence, if mercuric ion should be present, ammonium sulphide must be used (even when cupric sulphide is also present in the precipitate). In this case it is only necessary to take into consideration the fact that a little cupric sulphide may be present in the sulphides of Group VI., and that under certain conditions only cupric sulphide is dissolved.

This takes place the more readily the more polysulphide the ammonium sulphide contains (*i.e.* the more yellow it is). But even when sodium sulphide is used, some cupric sulphide may be dissolved when arsenic or stannic sulphide is present, since soluble double sulpho-salts of the arsenic or tin with copper and sodium may be formed.

25. If the precipitate produced by hydrogen sulphide is not completely washed, and portions of a solution containing metal ions of Group IV. still adhere to it, these ions may be precipitated, during the treatment with ammonium (or sodium) sulphide, in the form of sulphides, which (even in the absence of members of Group V.) will remain insoluble and be mistaken for Group V., or else be mixed with it and so cause errors or, at all events, unnecessary work.

26. If the solution to be treated with hydrogen sulphide contains mercuric ion, in addition to stannic ion, it may, under certain conditions, when directly treated with ammonium sulphide, retain the whole of the mercury, together with the tin, in solution (presumably owing to the formation of a double sulphide or double sulpho-salt. Th. Wilm, *Zeitsch. anal. Chem.*, 28, 99). In like manner, on treating the sulphide precipitate produced by hydrogen sulphide with ammonium sulphide, the mercuric sulphide will dissolve more or less completely when the liquid is diluted with *water*. If a 10 per cent. solution of ammonium nitrate is used instead of water, the solution of the mercuric sulphide is prevented. But a portion of the stannic sulphide will then remain undissolved among the members of Group V. (A. R. Cushman, *Chem. Zentr.*, 1893, II., 775), which point must be taken into consideration in Sec. 168.

Not infrequently when acid solutions are treated with hydrogen sulphide, or also when the ammonium sulphide, which has been used for extracting any metallic sulphides of the sixth group, is decomposed with hydrochloric acid, precipitates are obtained which have almost the appearance of pure sulphur, so that it is doubtful whether they should be tested for metals. In such cases (when *considerable* amounts of sulphur have not separated in agglomerated masses, as happens when hydrogen sulphide is introduced into hot solutions containing much strong nitric acid or *aqua regia*, or on acidifying ammonium sulphide solutions rich in polysulphides), the result is attained with certainty by the method described in the preceding analytical course of shaking the liquid with benzene or petroleum spirit, which will dissolve the sulphur but not the metallic sulphides. This obviates the necessity (excluding the above-mentioned exceptional cases) of using the former customary but more tedious method of determining whether cations of the fifth or sixth group were present, by treating the washed still moist precipitate with a solution of bromine in hydrochloric acid, or with hydrochloric acid containing potassium chlorate, diluting and filtering the liquid, heating it to remove the free bromine, and again testing it with hydrogen sulphide. If it is desired to make a further direct examination of the precipitate which has been freed from sulphur by means of benzene or petroleum spirit (as may be necessary in the case of small precipitates), the liquid with the precipitate in suspension should be poured on to a moistened filter, the aqueous solution drained off, and absolute alcohol poured on to the filter. After the alcohol mixture has drained off, the precipitate is washed, first with alcohol and then with water, and used for the further examination. **27.**

Of the rarer elements, the following are precipitated as sulphides from an acid solution by means of hydrogen sulphide: Palladium, rhodium, osmium, ruthenium, iridium,[1] germanium, molybdanum, tellurium, selenium, and possibly thallium.[2] **28.**

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[1] The platinum ore metals are precipitated with difficulty by hydrogen sulphide. The gas must be introduced for a long time into the hot liquid if precipitation is to be effected. With regard to the separation of these metals, see Mylius and Förster (*Ber.*, 1892, 665), and also Mylius and Mazzucchelli (Sec. 86).

[2] Tungsten and vanadium will not be found in the precipitate when it was produced in an acid solution by means of hydrogen sulphide; but they

Separation of sulphur, however, through the decomposition of hydrogen sulphide in acid solution is caused by the following compounds of rarer occurrence: Manganese and cobalt compounds containing the metal in a higher stage of valency than the divalent condition, vanadates (accompanied by a blue coloration of the liquid), sulphites, thiosulphates, nitrites, chlorites and hypochlorites, bromates and iodates.

On treating the precipitate with ammonium or sodium sulphide, the sulphides of the following elements are dissolved (with the sulphides of arsenic, antimony, etc.): Germanium, iridium, molybdenum, tellurium, and selenium; whilst the sulphides of palladium, rhodium, osmium, and ruthenium, and also of any thallium which may possibly be present here, remain undissolved (together with the sulphides of lead, bismuth, etc.).

Notes on Sec. 167.

29. The method described in (124) for the separation of gold and platinum from the rest of the metals of Group VI. depends upon the volatility of the chlorides of arsenic, antimony, and tin, and also of the sulphur of the sulphides in a current of chlorine. Since the application of such a method is disagreeable and unsuitable for qualitative analysis, R. Fresenius proposed to replace the chlorine by a current of air charged with the vapours of ammonium chloride and nitrate. It is an essential condition of this method that both the precipitate and also the ammonium salts should be thoroughly dry before they are mixed. If, in spite of this, the mixture appears moist, especially after standing for some time, it must again be dried at 100°. Explosions may readily occur if the mixture is dried on the sand bath or on an iron plate. The residue of gold or platinum in the boat does not always show a distinct metallic lustre. Moreover, frequently it only really dissolves after *long* heating with *aqua regia.* This must be borne in mind if the noble metals are not to be overlooked

30. If the metals of rarer occurrence have also to be taken into consideration in a precipitate of the sulphides of Group VI., it should be noted that if there is also a question of iridium being present, the same procedure must be followed as when the presence of gold and platinum has to be taken into account. Iridium also remains in the residue after the heating with ammonium chloride and nitrate. All the other sulphides are volatilised as chlorides.

may be present if the liquid was treated first with ammonium sulphide and then with acid in excess, in which case, however, the sulphides of nickel or cobalt would also be found among those of the fifth and sixth groups. Thallium, which under ordinary conditions is not precipitated from acid solutions by hydrogen sulphide, may be precipitated in association with arsenious or antimonous sulphide in the form of a solid solution.

On fusion with sodium nitrate and carbonate (120) and extraction of the fused mass with cold water, germanium, tellurium, selenium, and molybdenum are also dissolved, together with the arsenic as anions.

The methods of detecting the rarer elements in the solution, and of detecting iridium in the sublimation residue are given in Secs. 93 to 98.

Notes to Sec. 168.

The separation of the sulphides of the fifth from those of the **31.** sixth group cannot always be completely effected by means of ammonium or sodium sulphide, especially in a single treatment; hence, under certain conditions, traces of the sulphides of the sixth group may be found among the sulphides of the fifth group; in particular, small amounts of gold and platinum sulphides may easily be left among them, and this had also to be taken into consideration in Sec. 168, especially (133). Since the solution of platinum nitrate (which is obtained when the platinum sulphide was precipitated in the cold) is brown, the presence of platinum among the members of the fifth group may sometimes be recognised by the fact that the solution obtained by heating the sulphides with nitric acid has a brown colour. On evaporating such a brown solution, igniting the residue, and heating it with nitric acid, metallic platinum is left, whilst the oxides of the other metals dissolve.

The separation of mercuric sulphide from the other members of **32.** the fifth group by boiling them with dilute nitric acid is not successful unless the precipitate of sulphides was washed completely *free from chloride*, for otherwise *aqua regia* is formed, which then oxidises and dissolves the mercuric sulphide. Oxidation of mercuric sulphide also takes place when the mercuric sulphide is boiled for too long a time with nitric acid which is not sufficiently diluted. Under these conditions, however, the mercuric sulphide is not directly dissolved, but is first converted into the *white compound*, $2HgS+Hg(NO_3)_2$ (Sec. 74, 3). On the other hand, traces of the other sulphides may readily be masked by the sulphur which separates during their solution, this sulphur frequently appearing black, even in the absence of mercuric sulphide. With a little practice it soon becomes possible to determine, especially from the specific gravity, whether a permanent dark residue left after the boiling with nitric acid is mercuric sulphide or only coloured sulphur. If, therefore, it is a question of not overlooking small quantities of the former, every dark residue must be examined as in (133).

An insoluble residue left after the boiling with nitric acid may **33.**

contain the sulphides of gold or platinum in addition to mercuric sulphide, and also tin oxide, especially when the sulphide precipitate contains stannous chloride, or when colourless ammonium sulphide was used for the separation of Groups V_2. and VI.; tin may also readily occur in the residue, for the reason given on p. 804, No. 26, whilst the residue may contain lead sulphate formed from lead sulphide. Lastly, when mercury is present, more or less cadmium (all if it is only a small amount) may be left in the residue undissolved by nitric acid. Hence, under certain conditions, it is necessary to test a residue insoluble in nitric acid for all these substances. This tedious procedure, however, is only necessary when the elements in question have not been found without such tests (if they have to be taken into consideration at all, which is not usually the case with gold and platinum). The attention of beginners, however, should be directed to the fact that the occurrence of an insoluble precipitate may be accounted for in this way, even when mercuric sulphide is not present.

34. For the detection of lead ion the addition of a certain excess of sulphuric acid is required, in order that the solubility product may be exceeded with certainty, even with a low concentration of the lead ion; at the same time, the solubility of the lead sulphate is increased by the presence of nitric acid, and, hence, when a precipitate is formed, the nitric acid must be evaporated on the water bath. If an absolutely dry mass is left, an excess of sulphuric acid was not present, and more of that acid must be added. At the same time, too large an excess of sulphuric acid must be avoided, because otherwise too large an amount of ammonia will be required in the subsequent treatment of the liquid. If, therefore, after evaporation on the water bath, much thick oily liquid is left, from which nitric acid fumes no longer escape, it is better to expel a considerable proportion of the sulphuric acid by heating the residue more strongly.

With regard to the prevention of bismuthyl pyrosulphate being mistaken for lead sulphate, *cf.* Sec. 76, 10. To prevent this happening, immediate filtration of the residue from the evaporation, after dilution with water, is advisable.

A special test for lead in the precipitate produced by sulphuric acid is necessary, since it might be due to barium sulphate, which, owing to insufficient washing of the sulphide precipitate, could have separated at this stage.

35. If the first hydrogen sulphide precipitate was not thoroughly washed, and the solution contains iron ions (or if it is a question of the case mentioned on p. 611, footnote 1), the precipitate produced by ammonia will contain ferric hydroxide (possibly in addition to bismuth). It will then have a yellowish to brownish-red colour, and must be tested for bismuth. But, apart from this, it is also possible, under certain conditions, for a precipitate to be produced by ammonia, even in the absence of bismuth, *e.g.* when mercuric ion has dissolved during the treatment of the sulphide precipitate (*cf.* No. 22), or when the separation of lead ion as sulphate has not been complete (*cf.* No. 34), or also when aluminium or chromic ion is present, and the first hydrogen sulphide precipitate has not been thoroughly washed.

Hence, even when a pure white precipitate is obtained, it must always be specially tested for bismuth by dissolving it in a little hydrochloric acid, and adding a large amount of water.

In the separation of cupric ion from cadmium ion by means of **36.** potassium thiocyanate, it should be noted that only cuprous thiocyanate is sufficiently insoluble, so that it is necessary to add enough of a reducing agent to convert the whole of the cupric ion into the monovalent condition. The colour of the copper precipitate is a good criterion whether this object has been attained. The precipitate is relatively very fine, and easily passes through the filter; hence it should be allowed to subside completely (130), and care should be taken during the filtration not to disturb it, or to transfer any material quantity of it to the filter. In other cases, in the subsequent precipitation of the cadmium ion by means of hydrogen sulphide a brownish precipitate is often obtained instead of a pure yellow one, so that it remains doubtful whether any cadmium ion is present. On the other hand, the presence of cadmium may also be rendered doubtful by a separation of sulphur on the addition of hydrogen sulphide (129). Such separation may take place when sulphur dioxide is used as reducing agent and the excess thereof is not boiled off prior to the addition of hydrogen sulphide water. It should be borne in mind that the detection of cadmium ion is less sharp when the liquid contains a considerable amount of free hydrochloric acid.

But not only may the presence of cupric ion cause a precipitate obtained in (129) to be of a dark colour, but other members of Group V. may also have a disturbing influence here, should they have been overlooked in the examination, or have been incompletely separated. If, however, a black precipitate is obtained in (129), a further examination must be made. If cupric ion is present, or there is reason to infer that it is the cause of the dark coloration, the precipitate is washed, and tested either by means of potassium cyanide solution, which will dissolve cupric sulphide and leave a residue of yellow cadmium sulphide, or by boiling it with dilute sulphuric acid, which will dissolve cadmium sulphide, and treatment of the filtrate from the residual cupric sulphide with hydrogen sulphide water, whereby the cadmium ion is re-precipitated as sulphide (*cf.* Sec. 77, 4, and Cushman's method there described).

If this test is inconclusive, or if no copper ion is present, and the dark coloration is thus due to the presence of another metal, the dark precipitate obtained in (129) is carefully washed, and again cautiously treated with dilute nitric acid as in (126). If mercuric sulphide remains undissolved, a small portion of the nitric acid solution is tested for cadmium ion by means of hydrogen sulphide. If a yellow precipitate is not obtained, or if no mercuric sulphide was left undissolved, the nitric acid solution should be tested by the following method described in No. 37.

37. In addition to the methods described in the analytical course, the following process for separating the ions of lead, bismuth, copper, and cadmium also gives very trustworthy results. The nitric acid solution is treated with sodium carbonate, so long as a precipitate is produced, and then with excess of potassium cyanide solution, and heated. This causes lead and bismuth ions to be precipitated as carbonates, whilst copper and cadmium ions are obtained as potassium double cyanides in solution. The former may be readily separated (after thorough washing) by means of sulphuric acid, whilst the latter are separated by heating the potassium cyanide solution with excess of hydrogen sulphide, and re-dissolving any cupric sulphide, simultaneously precipitated, by the addition of a little more potassium cyanide. Cadmium ion may be recognised by the presence of an insoluble yellow precipitate of cadmium sulphide. The filtrate is treated with hydrochloric acid; a black precipitate of cupric sulphide indicates the presence of cupric ion. Since hydrocyanic acid is liberated on the addition of hydrochloric acid, *the operation must be carried out in a fume cupboard.*

38. If there is reason to suppose that the precipitate, which contains the sulphur compounds of the fifth group, also contains the sulphides of palladium, rhodium, osmium, ruthenium, and thallium, in addition to the sulphides of copper, bismuth, etc., a small portion of the precipitate is tested spectroscopically for thallium, and the remainder examined by the following method :—

It is fused with potassium hydroxide and chlorate, the mass being finally heated to redness, and then allowed to cool and treated with water. The solution may then contain, in addition to potassium plumbate, potassium perosmate and ruthenate, and, in the latter case, will be of a deep yellow colour. By introducing carbon dioxide the lead ion may be precipitated as carbonate. On then carefully neutralising the filtrate with nitric acid, black ruthenium sexquioxide is precipitated, and, if the filtrate is treated with more nitric acid and distilled, osmium tetroxide will be obtained in the distillate. When the insoluble residue from the treatment of the fused mass with water is gently ignited in a current of hydrogen (in which process any cadmium present might volatilise), and then cautiously treated with dilute nitric acid, rhodium and palladium are left, whilst copper and any lead, etc., still present are dissolved. The palladium may then be dissolved by *aqua regia*, whilst the rhodium remains undissolved. For the further examination of the metals thus separated, reference may be made to Secs. 79 to 81 and Sec. 86. When the process outlined above is used, a special portion of the sulphide precipitate must be tested for mercury.

Notes to Sec. 157 (56), (63), (64). 65), and *to Sec.* 169.

In testing for cations the presence of organic acids may, in many respects, have a disturbing influence. **39**

1. Because the precipitation of chromic and aluminium ion by means of ammonia may be prevented by the anions of many organic acids, owing to the formation of complexes, and, in the same way, that of manganous ion by ammonium sulphide may be affected. These cations are then no longer present, or not completely so, in the ammonium sulphide precipitate, they can, therefore, be overlooked, and, further, they can have a disturbing influence on the detection of the cations of Groups I. and II. Thus precipitates are still formed, under certain conditions, with ammonium carbonate, but especially with sodium ammonium hydrogen phosphate, even in the absence of members of the second group, and possibly by aluminium ion, although no precipitation was caused by ammonia or ammonium sulphide ; thus, in testing for alkali ions fixed residues are obtained, even when members of Group I. are not present. These precipitates and residues also interfere with the detection of cations of Groups II. and I., since it is assumed in this course that other substances are no longer present in the respective places, and the conclusions drawn from the phenomena which appear are only valid when based on this assumption (*cf.* No. 12 and No. 64).

2. Because, in testing for barium, strontium, and calcium ions under certain conditions, especially when too little ammonia or ammonium carbonate was added, the organic acid salts of alkaline earth metals are precipitated with the carbonates (or instead of them), and consequently mistakes may be made in the further treatment of the precipitate, in that the anion of the organic acid may still be found in the solution produced by hydrochloric or nitric acid.

3. Because they have a disturbing influence on tests for alkali metals. Thus, for example, platino-hydrochloric acid produces in solutions of sodium salts of organic acids (cinnamic acid, etc.), precipitable by acids, precipitates which in the yellow solution may be confused with potassium platinochloride.

It is therefore advisable, in the examination of members of Groups I. to III., to take the possible presence of organic acids into consideration.

In the simple course this is mentioned in (56, footnote 2), (63), and (65).

In the case of mixed compounds, organic acids or their ions, if present, should be destroyed before testing for members of Groups I. to IV.; this should be done in two separate portions by different methods, as described in Sec. 169. It should be noted, further, that if the original substance is completely soluble in water or acid, and contains no members of Groups V. or VI., it may be used directly for the fusion with alkali carbonate and nitrate, or for heating with sulphuric acid, and that its solution need not first be evaporated.

The destruction of organic substances by means of fusion in the portion in which members of Groups II. to IV. are to be detected must be effected in a platinum crucible, because, if a porcelain crucible is used, silicic acid and aluminium may be taken up from the glazing. For the purpose of solution, therefore, the fused mass should be transferred from the platinum vessel to a glass or porcelain vessel before the addition of hydrochloric acid, to avoid the possibility of platinum dissolving. Despite this fact, the fused mass occasionally absorbs a little platinum (especially if caustic alkali has been produced from the potassium nitrate), and thus has a disturbing influence on the detection of metal ions, particularly of nickel and cobalt ions.

Notes to Sec. 157 (56), *Sec.* 160 (84), *and Sec.* 170.

40. Precipitation with ammonium sulphide should be employed for the separation of the members of Groups III. and IV. from those of

Group II. (provided that, in addition to the latter, there are not also present phosphate, oxalate, borate, silicate, fluorine, and possibly tartrate or citrate ions). Care must, therefore, be taken to see that neither the ammonia nor the ammonium sulphide contains carbonate (owing to the absorption of carbon dioxide from the air, and that the ammonium sulphide is also free from sulphate (produced by oxidation by the oxygen of the air). Otherwise, even in the absence of the anions mentioned, *i.e.* of substances completely soluble in water, barium, strontium, and calcium ions may be precipitated as carbonates or sulphates. It is then useless to attempt to detect the members of Groups III. and IV. in such a precipitate.

In doubtful cases, therefore, a test should be made as to whether the ammonia or ammonium sulphide gives a precipitate with barium chloride.

Magnesium ion may also be precipitated (incompletely) as hydroxide by means of ammonia free from carbonate, if ammonium salts are not present in sufficient quantity to check the dissociation of the ammonium hydroxide present in the ammonia solution (p. 34). **41.**

If, therefore, the solution does not contain so much free acid that a sufficient quantity of ammonium ion passes into the solution on neutralisation with ammonia, a corresponding quantity of ammonium chloride must first be added.

If ammonium sulphide is added to the solution which has not yet been neutralised with ammonia, it is decomposed, so that (apart from the unnecessary and unpleasant evolution of hydrogen sulphide) under certain conditions the precipitation of the members of Group IV. does not take place, or is only incomplete. **42.**

If *too much* ammonia is added, aluminium, and possibly also chromium, may remain in solution as anion, and have the disturbing influence described in No. 39, 1, on the detection of members of Groups I. and II.

As it is frequently important in determining whether members of Group III., or (in the presence of the anions of phosphoric acid, etc.), those of Group II. are present, to ascertain whether ammonia alone produces a precipitate, the test as to whether members of Groups III. and IV. are present at all (as given in (137)) is made by adding first ammonia alone and then ammonium sulphide. It is, of course, assumed that if a precipitate was previously produced by hydrogen sulphide, the excess of the gas was removed from the filtrate before ammonia is added. **43.**

This is not necessary in the actual precipitation (141) or (151);

for this reason a precipitate (of sulphide) may, under certain conditions, be produced there by ammonia, whereas in (137) no precipitate was produced by ammonia alone. In (141) or (151) ammonia may produce a precipitate of a different colour from that in (137).

To be certain that the hydrogen sulphide was removed in (137), the liquid is oxidised, after boiling, by heating it with a little nitric acid.

44. In the tests in (137) certain conclusions may be drawn from the colour of the liquid, or any change of colour on boiling it with nitric acid. Thus, it is a matter of importance in the course in question whether the coloration indicates chromic ion (violet or green, in any case green after boiling), *i.e.* whether (141) or (150) should be followed. A red coloration points to the presence of cobalt ion, and a light green one to that of nickel ion. But the last two colours, which are reciprocally complementary, can almost neutralise each other, and even if a distinct coloration is not perceptible, there is still the possibility that cobalt and nickel ions are present.

A reversion from colourless to yellow points, as a rule, to ferrous ion.

45. If chlorine and iodine ions are present simultaneously in the solution, iodine may be liberated on boiling with nitric acid, and a yellow coloration be produced. The iodine may be detected by its colour.

In this case, a *dark* precipitate of nitrogen iodide may be formed on the addition of ammonia (even in the absence of iron, aluminium, and chromium ions, as also of phosphates, etc., together with the cations of the second group). To avoid this, the liquid is evaporated on the water bath before the addition of ammonia, in order to expel iodine or iodine chloride, next diluted, and only then neutralised with ammonia.

46. The conclusion that when ammonia produces no precipitate no cations of Group II. can be present, together with the anions of oxalic acid and boric acid (138), is not unconditionally certain, since magnesium oxalate is only precipitated after some time, and never completely, from hydrochloric acid solution by means of ammonia, and since the precipitation of the alkaline earth borates may be influenced or inhibited by the presence of ammonium salts.

If, therefore, the conditions in the preliminary test (137) are slightly different from those in the definite precipitation (141) or (150), the substances mentioned may, in the one instance, be absent from the precipitate produced by ammonia and ammonium sulphide, and in the other be present therein.

In the presence of aluminium or chromic ion, small quantities of the ions of alkaline earth metals may pass into the ammonium sulphide precipitate, if the frequently mentioned anions (the ions of phosphate, etc.) are absent.

For these reasons it is always wiser in very exact analyses to adopt the complicated course (150).

47. The reason for the statement made in (140) that, in the event of the colour of the solution indicating the presence of chromic compounds, the comprehensive course (143) should be adopted, is that in the presence of chromic ion in the separation with sodium hydroxide (143) the zinc ion may be completely precipitated *with* the chromic hydroxide (p. 259), and therefore would not be detected in the simple course in the usual place. If the simple course has been chosen, however, and chromic ion is found in (146), the precipitate containing chromium must be tested again for zinc ion as in (146, $\gamma\gamma$), provided zinc ion has not been detected by hydrogen sulphide in the alkaline solution.

48. It is stated in (141) and (151) that the liquid should be shaken until the precipitate begins to separate in flocculent form, and should then be allowed to stand in a warm place.

This is necessary, because the sulphides separate at first in colloidal form or in fine suspension ; consequently the liquid will be turbid when passing through the filter, if it is filtered immediately after precipitation. The precautionary measures given, as also the addition of a corresponding quantity of ammonium salt, will cause a separation which permits of clear filtration (*cf.* pp. 31 to 36, and p. 44).

If the liquid has to stand in a warm place for some time, it is best to keep it in a loosely-corked boiling flask, in order to decrease the oxidising action of the air as far as possible.

49. Nickel sulphide dissolves to a slight extent in excess of ammonium sulphide, owing to the formation of sulpho-salt ions. In consequence of this, the precipitation of nickel ion by means of this reagent is, under certain conditions, incomplete. This may be recognised by the brownish to dark brown colour of the filtrate. Such a colour always points to the possible presence of nickel ion (or vanadium ion, which behaves in the same way). Platinum ion, which may have been taken up on the destruction of the organic substances (*cf.* the end of No. 39 and No. 52), can also produce a brownish coloration. The extent to which the nickel remains in solution as sulpho-salt ion depends also on the amount of ammonia and ammonium salts contained in the solution (Sec. 59, 5).

If such a brown filtrate is obtained, it must be freed from nickel ion before it can be tested for members of Groups I. and II. This is done by acidifying it with acetic acid and heating it, whereby nickel sulphide (possibly also dissolved platinum or vanadium sulphide) separates in such a form that it can be separated by filtration.

The solvent action of ammonium sulphide on nickel sulphide is also shown when the latter is washed with water containing ammonium sulphide. For this reason, it is stated in (141) and (151) that only a very small quantity of ammonium sulphide should be added to the washing water.

The object of making such an addition at all is to prevent oxidation of the moist sulphide by atmospheric oxygen (No. 22) during washing.

50. The separation of cobalt and nickel from the other constituents present in the ammonium sulphide precipitate (apart from certain amounts of silicon dioxide, calcium fluoride, and calcium oxalate (153)) depends upon the solubility of their sulphides in hydrochloric acid. This rule, however, is not unconditional, and the hydrochloric acid must, therefore, be *diluted* and treated in the cold. Nevertheless, small quantities of nickel and cobalt sulphides are dissolved.[1] If the air is allowed to have an oxidising action, the solution is materially promoted. For this reason, hydrogen sulphide water should be used for dilution.

If the ammonium sulphide precipitate is not black, *i.e.* does not contain nickel or cobalt sulphide, or at least only contains small quantities of these substances, it may be treated with hot hydrochloric acid which has not been further diluted, since only then (142, *a*) can it be completely dissolved.

51. In order, however, to effect as complete solution of the other substances as possible when nickel or cobalt is present, a sufficient quantity of hydrochloric acid diluted with hydrogen sulphide water must be used, since at least one equivalent of hydrochloric acid must be present for each equivalent of the respective metals present. It is, therefore, advisable, if a fairly large residue (undissolved in the dilute hydrochloric acid) remained on the filter (147), to treat it again with a fresh quantity of the mixture of one part of dilute hydrochloric acid and four parts of hydrogen sulphide water. Even then, part of the remaining substances may escape solution (especially ferrous sulphide), owing to portions of the ammonium sulphide precipitate being enveloped in separated sulphur.

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[1] These will be present in the precipitates produced by sodium hydroxide (149), (159), which should be specially noted when no manganese, iron, or chromium is found in such a precipitate. The chromium may also dissolve, forming a blue solution (Sec. 60, 1); a black precipitate is then obtained in testing for zinc ion by means of hydrogen sulphide.

In order, therefore, to obtain the portion containing nickel and cobalt free from the other substances soluble in hydrochloric acid, it is not sufficient to wash the residue well, but, after volatilising the sulphur, it must be dissolved in *aqua regia* (care being taken to continue the treatment until everything has dissolved, because the ignited precipitate will have become very dense), and any ferric ion present then precipitated by means of ammonia.

If any platinum has been taken up by the fused mass in the **52.** destruction of organic substances (*cf.* end of No. 39), or if the precipitation with hydrogen sulphide (113) was not complete, portions of members of Groups V. and VI. may have passed into the ammonium sulphide precipitate (141) or (151). These will remain undissolved on treatment with hydrochloric acid, and may be mistaken for nickel or cobalt sulphide, or have a disturbing effect on their detection. If this is thought to be likely, or if, in the detection of nickel or cobalt ion, unusual phenomena occur (*e.g.* if no nickel and cobalt ions are found, although a black residue insoluble in hydrochloric acid was left, and no ferrous sulphide was present), the *aqua regia* solution obtained in (148) or (153) is freed from nitric acid by evaporation, *diluted*, and then treated with hydrogen sulphide, and any precipitate filtered off; the filtrate is tested to see whether a precipitate is produced at all by ammonia and ammonium sulphide. (If it is probable that platinum ion is present, this can, if necessary, be separated by the addition of ammonium chloride and evaporation to a small residue.) Of the members of Group V. which may be found here, cadmium and lead ions enter first into consideration, because they are not precipitated completely by hydrogen sulphide from strongly acid solution.

Since part of the sulphides of Group V. can be dissolved on treatment with hydrochloric acid (142) or (152) (especially if it was not sufficiently diluted), they can also have a disturbing influence on the examination of the solution.

For instance, in testing with hydrogen sulphide for zinc ion (144), a black precipitate of lead sulphide may be produced in an alkaline solution. (It is dissolved in acid, the solution evaporated with sulphuric acid, the residue taken up with water containing sulphuric acid, the lead sulphate filtered off, and the filtrate tested again for zinc ion.)

In the same way, a precipitation may be caused by lead ion in testing the hydrochloric acid solution with sulphuric acid for barium, strontium, and calcium ions (155). If this appears to be the case, (which may be recognised by the precipitate becoming black on the addition of hydrogen sulphide water), the lead ion is precipitated, from a fresh sufficiently diluted sample of the hydrochloric acid solution of the ammonium sulphide precipitate, with hydrogen sulphide, and the test only then made with sulphuric acid.

53. If the original solution was not a pure aqueous one with a neutral reaction, any residue left on treatment of the ammonium sulphide precipitate with hydrochloric acid (153) may also contain silicon dioxide, calcium fluoride, calcium oxalate (and possibly also barium sulphate if the ammonium sulphide contained sulphate, or if sulphate was formed on exposure of the sulphide precipitate to the air, or during its solution) If the *simultaneous* presence of all these substances has to be taken into consideration, the procedure described in the course for substances insoluble in acid (199) or No. 83 in this chapter should be adopted. In testing for calcium oxalate, which is insoluble in the dilute acid, a portion of the unignited precipitate should be dissolved in strong hydrochloric acid.

54. The test with potassium nitrite for cobalt ion should be applied in not too dilute acetic acid solution. As a suitable method nickel and cobalt ions may be precipitated as carbonates with sodium carbonate, and the precipitate filtered off and dissolved in acetic acid. (The mineral acid solution could also be treated with sodium acetate, but in that case the liquid is easily rendered too dilute or the acidity is not sufficiently repressed.) It should be noted that, if all the ammonium salts have not been previously expelled in (118), the liberated ammonia may prevent the precipitation with sodium carbonate. The acetic acid solution may be tested with dimethylglyoxime for nickel ion (Sec. 59, 18), and with α-nitroso-β-naphthol for cobalt ion (Sec. 60, 18), instead of by the method described in (149).

55. In testing for manganous and chromic ions in (146) the precipitate is fused with sodium carbonate and potassium chlorate. If both are present together, the green or red colour of the manganate or permanganate masks the yellow colour of the chromate. In order to recognise the latter, the aqueous solution of the fused mass is boiled, in this case, with a little alcohol, which reduces the manganese compounds to hydrated manganese dioxide. So long as this brown compound is suspended in the liquid, however, the latter may very well appear yellow, even in the absence of chromate ion. Its colour therefore can only be really judged after the hydrated manganese dioxide has been removed.

To test for the degree of valency of the iron ion (145) (156) potassium *thiocyanate* and potassium ferrocyanide should be used. Potassium ferrocyanide may lead to errors in the case of small quantities of ferric compounds, owing to the fact that Prussian blue dissolves in excess of ferrocyanide solution. If, however, this reagent is used, it should only be applied drop by drop. **56.**

Notes on the differentiation of alkaline earth phosphates, borates, etc., from aluminium hydroxide and zinc sulphide, and on the separation of the anions of these alkaline earth salts, (86) to (89) and (156). **57.**

(*a*) It is stated in (86) in deciding whether the white ammonium sulphide precipitate (85) is, on the one hand, aluminium hydroxide or zinc sulphide, or, on the other, is the salt of an alkaline earth metal, that the original hydrochloric acid solution should be treated with concentrated potassium or sodium hydroxide solution in excess, and *boiled.* The latter is necessary, because calcium tartrate is soluble in excess of alkali hydroxide solution in the cold, but separates again on boiling. Under certain conditions this reaction may fail (p. 500, footnote 1). If this appears to be the case (it is indicated by a yellow coloration of the akaline solution on boiling), the precipitate obtained in (85) may have been calcium tartrate, even if no permanent precipitate was formed. If, therefore, the preliminary test showed the presence of organic substances, the precipitate obtained with ammonia (84, *bb*) is tested with resorcinol and sulphuric acid, to see whether it contains tartaric acid, and then tested for the cation according to (89, 5).

(*b*) It is stated in (88) that the hydrochloric acid solution should be rendered alkaline with ammonia in testing for phosphate ion (or for its separation), and that acetic acid should then be *immediately* added. This is necessary, because the alkaline earth phosphates only re-dissolve sufficiently readily directly after precipitation, while they are still flocculent. If they have become crystalline on standing, so much acetic acid is required for their solution, that the subsequent separation of ferric phosphate and of excess of ferric acetate can no longer be effected by boiling. In this case it would be better to dissolve such a precipitate by the addition of hydrochloric acid, and then carefully to add ammonia again, followed immediately by acetic acid. If the examination is correctly carried out, a colourless filtrate free from ferric ion will be obtained, after boiling.

(*c*) The following remarks may be made on 156 :—

1. The separation of phosphate and silicate ions by means of barium carbonate is only complete when these anions are separated as aluminium or ferric salts, that is to say, when an excess of the ion of at least one of these metals is present. Since a test for ferric ion can readily be made in a separate portion of the solution, an excess of ferric chloride is added after the test has been made. The presence of ferric ion may be recognised by the fact that ammonia produces a yellowish precipitate (not a white precipitate of $FePO_4$, as is the case without an excess of ferric ion).
2. Both in testing for iron ions and in precipitating them by means of barium carbonate, it is essential that they should be present in trivalent form. Consequently in (154) the hydrogen sulphide must be actually boiled away and the iron then oxidised with nitric acid (156). Before testing for ferric ion with potassium thiocyanate, the solution must be *cooled*, since in the presence of hot nitric acid either no reaction occurs in the presence of ferric ion, or a reaction taking place in its absence may be due to nitrite ion (Sec. 126, 11). The solution must also be cold when tested with potassium ferricyanide, as this will otherwise be decomposed, and a blue coloration may possibly appear, even in the absence of ferric ion.
3. Since there may be a disturbing influence if the liquid still contains much free acid before the addition of barium carbonate, so that on the one hand much barium ion dissolves, and, on the other, much carbon dioxide is evolved, which then causes a larger quantity of barium ion to dissolve as barium hydrogen carbonate (owing to which facts a very large precipitate would be produced in (158)), the liquid is first evaporated to a small residue, whereby chlorine or an excess of nitric acid is expelled (see 5 *infra*), and the liquid then nearly neutralised with sodium carbonate. The final evaporation is best carried out on the water bath, in order to avoid complete dryness, and the formation of a residue which dissolves with difficulty, even in acids.
4. The *separation* of trivalent cations and anions of phosphate, etc., from divalent cations is only effected by *barium carbonate*, whereas sodium carbonate also precipitates divalent cations.

When neutralising the liquid with sodium carbonate, care must, therefore, be taken to avoid precipitation taking place. Should this occur, however, the precipitate must be just re-dissolved in a little hydrochloric acid before barium carbonate is added.

5. Precipitation with barium carbonate must take place in the cold, as otherwise manganous ion might be simultaneously precipitated. Care should be taken that the solution is hot, after the neutralisation with sodium carbonate, and is then cooled. Manganese can pass into the precipitate in a higher stage of valency, if the liquid still contains nitric acid or chlorine, and these must, therefore, be expelled by evaporating the liquid to a small residue (see 3), preferably by preliminary boiling. In order that a precipitate absolutely free from manganese may be obtained, it must finally be thoroughly washed. Should manganese be present in the precipitate, however, it will have a disturbing influence on the detection of chromic ion in (157). In this case, it must be removed by boiling the aqueous solution of the fused mass with a little alcohol, as in (146) (*cf.* also No. 55 in this chapter).

It is stated in (143) and (157) that the sodium hydroxide solution must be freshly prepared from solid sodium hydroxide. This is necessary, because solutions kept in glass vessels always contain silicate or aluminate, so that in using them for the test for aluminium ion a positive reaction is obtained when the substance under examination is free from it. **58.**

It has been said in (159) that a precipitate insoluble in ammonium sulphide solution consists of manganous (or nickel or cobaltous) sulphide. Occasionally, however, iron ion is also found here, that is to say, when the hydrogen sulphide was not completely expelled in (154). It may also be due (if no iron ions were originally present) to the ferric chloride added, which was partly reduced to ferrous chloride by the hydrogen sulphide. In this case a black sulphide precipitate is obtained here, even if the first ammonium sulphide precipitate was not black. **59.**

Notes to Sec. 170.

Taking into consideration all the unprecipitated elements in the liquid which was filtered from the precipitate produced by hydrogen sulphide in acid solution, it will be found that the following metals must be contained in the precipitate, if the liquid was neutralised with ammonia after the addition of ammonium chloride, and then treated with ammonium sulphide in excess :— **60.**

(*a*) As sulphides: Cobalt, nickel, manganese, iron, zinc, uranium, thallium, indium, gallium.

(*b*) As oxygen compounds: Aluminium, chromium, beryllium, thorium, zirconium, the elements of the yttria earths, cerium, lanthanum, didymium, titanium, tantalum, niobium.[1]

The task of separating from one another all the elements possibly present here will probably never occur in practice, and so far as the ions of the rare earths are concerned, is not feasible by the usual methods of ordinary qualitative analysis. We therefore confine ourselves to the description of the most important methods of separation, by means of which smaller or greater groups of elements may be separated from the remainder, and to certain directions as to the method of treating these sub-groups.

1. The following process may be used for the separation of *tantalic, niobic*, and *titanic acids* · The precipitate produced by ammonia and ammonium sulphide is ignited, the residue fused [2] with potassium (or sodium) hydrogen sulphate,[3] the fused mass treated, when cold, with a large quantity of cold water, digested with it for a fairly long time without heating, and the solution filtered from the residue. The *residue* contains tantalic and niobic acids, possibly also silicon dioxide and a little undissolved ferric and chromic oxides. On fusing it with *sodium hydroxide* and a little *potassium chlorate*, a mass is obtained in which, on treatment with dilute sodium hydroxide solution, the chromate and silicate ions are rendered soluble, whilst sodium niobate and tantalate insoluble in sodium hydroxide solution are left, together with any ferric oxide which may be present here. The separation of niobium and tantalum is best effected by conversion into alkali fluorides or oxyfluorides (*cf.* p. 211). With regard to the further examination, *cf.* Secs. 53 and 54.

The acid solution, which contains the titanic acid, or at least the greater portion of it, in addition to the cations of the third and fourth groups, is treated in the cold with hydrogen sulphide, to reduce any ferric ion present, well diluted, and boiled *continuously*, while carbon dioxide is being introduced (*cf.* p. 199). The titanic acid present in the solution separates as a white precipitate, which may possibly contain zirconium.

If the solution is *too* acid, titanic acid may not separate completely on boiling. If, therefore, after boiling for several hours, the liquid still gives the hydrogen peroxide reaction for titanic acid, the excess of acid is *carefully* neutralised with ammonia (though the reaction must remain strongly acid) and the liquid boiled again.

In the process just described the tantalic acid and a portion of the niobic acid are precipitated by hydrolysis on treating the residue of the mass, after fusion with bisulphate, with water in the cold, but complete separation does not occur, because, on the one hand, the precipitating niobic acid carries down a considerable quantity of titanic acid, and, on the other, remains partly in solution. It is also possible, instead of dissolving in cold water the mass obtained in the fusion with alkali hydrogen sulphate, to dispense with what is only an incomplete separation of the three earth acids on dissolving the fused mass, and to precipitate them *together* at boiling point by means of hydrolysis, and then to separate them from one another as in Sec. 45, A. (In the absence of tantalic acid, niobic acid cannot be completely separated by boiling. The addition of a solution of sulphur dioxide promotes the separation of the earth acids on boiling.)

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[1] Only those portions of the niobic acid can be present here which redissolved on the first precipitation with hydrochloric acid, and on washing the resulting precipitate.

[2] It is allowed to cool from time to time, and a few drops of concentrated sulphuric acid added, to replace that which escaped.

[3] If the object under examination can contain rare earths, it is preferably fused with *sodium* hydrogen sulphate, to avoid the formation of sparingly soluble potassium double sulphates.

2. If the filtrate obtained after separation of tantalic, niobic, and titanic acids, or if a solution free from these acids is treated with ammonia, with the addition of ammonium chloride, after any ferrous ion present has been oxidised by boiling with nitric acid, and the slightly washed precipitate is dissolved in hydrochloric acid and the solution again treated with ammonia, the ions of *zinc*, *manganese*, *nickel*, *cobalt*, and *gallium* will be obtained almost completely in solution, whilst the *earths* will remain in the residue, together with the hydroxides of *iron*, *indium*, *uranium*, and *chromium*.

3. *Gallium ion* may be separated from *zinc*, *manganese*, *nickel*, *cobalt*, and *ferrous ions* by treating the hydrochloric acid solution with *barium carbonate* in the cold. By this means gallium ion is precipitated, whilst the other ions mentioned remain in solution. Gallium ion can be separated by means of potassium ferrocyanide in strongly acid solution from any aluminium ion which may have passed into the ammoniacal solution and have been precipitated, together with the gallium ion by means of barium carbonate (Browning and Porter, *Chem. Zentr.*, 1918, I., 950).

4. To separate the ions of aluminium and beryllium, as also chromic ion from ferric ion, the ions of indium and uranium, and the remaining members of the third group, their solution in hydrochloric acid is treated in the cold with concentrated *potassium* (*not sodium*) *hydroxide solution*.[1] By this means aluminate and beryllate ions, also, under certain conditions, chromite ion, are obtained in solution, whilst the ions of the other earths, together with iron, indium, uranium, and possibly chromic ions, are precipitated. If the alkaline liquid is diluted, filtered, and continuously boiled, *aluminate ion* (which can then be precipitated by ammonium chloride) remains dissolved, whilst any *chromite ion* present and the *beryllate ion* are precipitated as hydroxides (*cf.* p. 174). These last may be separated by fusion with *sodium hydroxide* and *potassium chlorate* in the same way as is usual with aluminium and chromic ions (Sec. 42, 3; *cf.* in regard to this paragraph also Sec. 55, 2).

5. Instead of the method of separation given in 2, 3, and 4, the precipitation of the rare earths as *oxalates* may in many cases be recommended for the separation of the ions of the *ceria and yttria earths* and of *thorium*

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[1] See also Sec. 43, 3.

from those of *zirconium*, *beryllium*, *aluminium*, *chromium*, and the *ions of the fourth group*. According to Hauser and Worth,[1] the separation is carried out as follows: The hydroxides obtained, *e.g.* on treating the filtrate in 1 with ammonia, are dissolved in $\frac{1}{4}$ to $\frac{1}{2}$-N-hydrochloric acid in such a way that for each 1 grm. of the earths 60 c.c. of the liquid are present, and the solution then treated as 60° with 40 to 50 c.c. of a 10 per cent. *oxalic acid solution*. The separation of the precipitate, which rapidly becomes crystalline, is complete after 12 hours, only *zirconium ion*, which, in accordance with Sec. 45, 5, is soluble in excess of oxalic acid, having dissolved with the aluminium ion, etc.; it can be separated with the aluminium ion from the ions of the other dissolved substances by precipitation with *sodium thiosulphate* (Sec. 40, 8, and Sec. 45, 8). *Zirconium ion* may then be separated from *aluminium ion* by precipitation with *alkali iodate* (Sec. 45, 11).

6. *Thorium ion* may be separated from the ions of *cerium*, *lanthanum*, and *didymium*, as also from the *yttria earths*, by treating the oxalates with a concentrated boiling solution of *ammonium oxalate*, diluting the liquid, and, when cold, filtering off the mainly undissolved (the ions of the yttria earths are slightly soluble in ammonium oxalate solution) oxalates of the four elements first mentioned. *Thorium oxide* is obtained by evaporating the solution, and igniting the residue; of the other methods (see Sec. 55, 4) for the separation of *small quantities of thorium ion*, that given in 4 (*d*) of that section is the most suitable.

7. The ions of *zirconium* and *thorium*, and also those of the *ceria earths*, may be approximately separated from the ions of the *yttria earths* (and also from beryllium and aluminium ions) by means of *alkali sulphate* (*cf.*, however, Sec. 55, 5). The neutral, or scarcely acid, solution is treated with crystalline potassium sulphate (or, if it is a question of the separation of the ceria ions from those of the yttria earths, preferably with sodium sulphate), boiled, allowed to stand for 12 hours and filtered, and the resulting precipitate of the double sulphates of potassium with zirconium and thorium (as also of the ceria earth metals) washed with a solution of potassium sulphate. From this solution ammonia precipitates the ions of the *yttria earth metals* (of beryllium and aluminium), which last may be separated from the ions of the yttria earths by means of oxalic acid (*cf.* 5). On repeatedly boiling the precipitate of the potassium double sulphates with water and a little hydrochloric acid, the greater portion of the *zirconium sulphate* will remain undissolved, whereas the ions of *thorium* (and of the ceria earth metals) dissolve, and may be precipitated from the solution by means of ammonia.

8. The ions of *thorium* and *zirconium* may be separated from those of the yttria earths of cerium and didymium by means of *sodium thiosulphate*, by adding it in slight excess to the slightly acid solution, and boiling it. Owing to the resulting hydrolysis, the ions of zirconium and thorium are precipitated as hydroxides, whilst the ions of the ceria and yttria earths remain in solution.

9. *Zirconium ion* may be separated from the ions of *thorium* and of the

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[1] *Zeitsch. anal. Chem.*, **47**, 389.

yttria earths by means of a slight excess of *hydrofluoric acid,* which precipitates the latter but not zirconium ion.

10. With regard to the separation of *cerium ion* from the ions of *lanthanum* and *didymium,* see Sec. 55, 7.

11. *Indium ion* is best separated from *zinc and iron ions* by means of *barium carbonate.* The slightly acid solution (hydrochloric acid) is heated with sulphur dioxide, to convert ferric ion into ferrous ion, and when cold, treated with freshly precipitated *barium carbonate,* air being excluded. If much iron ion is present, the operation must be repeated. The precipitate containing indium is dissolved in hydrochloric acid, and barium ion precipitated by means of sulphuric acid. Ammonia then precipitates *indium hydroxide* from the filtrate.

12. To detect *thallium ion* in the precipitate produced by ammonia and ammonium sulphide, a portion of the precipitate is dissolved in boiling dilute hydrochloric acid, and the solution treated with sulphur dioxide until any ferric ion present has been converted into ferrous ion, the free acid almost neutralised with ammonia, and the solution tested with potassium iodide. Any precipitate produced should in any case be spectroscopically examined.

Notes to Sec. 157 (62) *and* (63) *and to Sec.* 171.

If the filtrate from the precipitation with ammonium sulphide is kept for some time, sulphate ion may be formed in it, owing to the action of air, whereby barium ion and possibly also strontium ion may be precipitated and escape detection. If, therefore, this filtrate cannot be used at once, it should be preserved in an almost filled and well-corked flask, or the ammonium sulphide should be removed. This can be done either by acidification with hydrochloric acid and boiling until the sulphur agglomerates, or, better, by shaking the liquid with powdered lead oxide, or, best of all, by heating on the water bath (Bogdan, *Zeitsch. anal. Chem.,* 44, 564). The liquid is then filtered from the sulphur, or from the mixture of lead peroxide and lead sulphide. **61.**

The precipitation of barium and calcium ions as carbonates is **62.** influenced by the presence of large quantities of ammonium salts, because the latter check the dissociation of the ammonium carbonate. On the other hand, a small quantity of ammonium salts is essential to prevent the precipitation of magnesium ion. Consequently, any large quantity of ammonium salts must be expelled by ignition, but it must be taken into consideration that small quantities of barium and calcium ions escape precipitation as carbonates, and they should therefore be removed with ammonium sulphate or oxalate before a test for magnesium ion is made with sodium ammonium hydrogen phosphate, since otherwise they may produce precipitates of phosphate. They may also have a disturbing influence on tests for alkali metal ions.

63. In the case of simple compounds, calcium sulphate solution affords a means of deciding whether barium, strontium, or calcium ion is present. Since, however, in the presence of much calcium ion the precipitation of barium or strontium sulphate by means of calcium sulphate may be entirely inhibited, this reagent cannot be used to obtain a definite decision in the case of mixed compounds (Sec. 34, 5, and Sec. 35, 3). With regard to a process for the detection of strontium ion, even in the presence of barium ion, by means of calcium sulphate solution, *cf.* Theodora P. Raikow, *Zeitsch. anal. Chem.*, **57**, 164.

Apart from the process given in the course of analysis, the methods mentioned in Sec. 38 may be used. It is essential in their application that the conditions given there be strictly observed.

Notes to Sec. 172.

64. The test for magnesium ion by means of sodium ammonium hydrogen phosphate is characteristic, provided it is realised that only a crystalline precipitate proves the presence of magnesium ion. It must be clearly understood that nearly all cations previously separated can yield insoluble phosphate precipitates. If, therefore, a non-crystalline precipitate is obtained, it is necessary to reflect in the case of which of the cations already found the precipitation may have been incomplete, and to apply tests for these (or to remove them) before making a decisive test for magnesium ion, or before testing for ions of the alkali metals. With regard to the most frequent case, *i.e.* the presence of traces of aluminium, barium, or calcium ion, the necessary instructions were given in (167). Of the other cations which may occur here, reference must in particular be made to tin ion, which is apt to be incompletely precipitated by hydrogen sulphide, and gives no precipitate with ammonium sulphide or, if present in small quantity, with ammonium carbonate, but yields a precipitate with phosphate ion. If, therefore, tin ion has been detected with hydrogen sulphide, and if an unusual precipitate has been obtained in (167), a test should be made to see whether a residue of tin cannot be separated on renewed treatment with hydrogen sulphide, and this filtrate only then tested for magnesium ion or the ions of alkali metals.

The liquid, filtered from the precipitate produced by ammonium sulphide, may contain, not only the ions of the alkaline earths and alkalis, but also a little *nickel ion*, *vanadium ion*, and that portion of the *tungstate ion* which was not precipitated at first by hydrochloric acid. The three last are present as sulphides dissolved in excess of ammonium sulphide solution, and are precipitated as such when the liquid is just acidified with acetic acid or hydrochloric acid. If the precipitate is filtered off, washed, dried, fused with sodium carbonate and sodium nitrate, and the fused mass treated with water, a residue of *nickelous oxide* is left, whilst *potassium vanadate* and *potassium tungstate* dissolve. The vanadic acid may be separated from this solution by means of solid ammonium chloride, and tungstic acid by evaporation with hydrochloric acid, and treatment of the residue with water; both acids may then be further examined (Secs. 68 and 98). **65.**

Notes to Secs. 157 (66) *and* 173.

66. No decision can be obtained as to whether potassium or sodium ion is present by testing the residue left after expelling the ammonium salts, even in the absence of all other cations, if, on ignition, the anions of non-volatile acids or acids which volatilise with difficulty (phosphoric acid, boric acid) are left.

If, therefore, an ignition residue is left it must be definitely concluded that such anions are not present. The anions mentioned, and also others, may have a disturbing influence on the individual tests for potassium or sodium ion. They can, for example, on the one hand, like sulphate ion, form acid salts in the residue from the ignition, or, like phosphate ion, cause an acid reaction, which will interfere with the reaction for sodium ion by means of dipotassium dihydrogen pyroantimonate. A white flocculent precipitate of antimonic acid is then formed, even in the absence of sodium ion, so that the doubt may exist as to whether a sodium precipitate has been formed. On the other hand, even on prolonged ignition, some of the ammonium may be retained by the phosphoric acid, and may lead to errors when testing for potassium ion.

Such disturbing anions must, therefore, be removed before testing for alkali metal ions. Borate ion has a disturbing influence on the detection of potassium as potassium hydrogen tartrate (Sec. 139, 5).

67. Care must be taken when noting whether a residue, stable on ignition, is left, because the salts of the alkali metals melt readily, and may, therefore, easily be overlooked. *Too small* a portion therefore should not be evaporated in this test, and the heating not increased *above* the necessary degree, but the ammonium salts must be completely expelled, and the behaviour noted on cooling and again heating the platinum dish (or cover); note must also be taken whether on heating, the flame is coloured (*cf.* No. 6).

68. Before magnesium ion can be removed in (170) by means of barium or calcium hydroxide, the ammonium salts must be expelled, since otherwise there is the danger that only ammonia will be liberated and an insufficiently high concentration of hydroxyl ions obtained, and consequently the magnesium ion will not be completely separated as magnesium hydroxide.

69. In removing disturbing anions, magnesium ion or the cations of Groups III. and IV., as in (170), the use of unnecessary quantities of barium chloride and barium or calcium hydroxide should be avoided. Nevertheless, comparatively large precipitates are not infrequently obtained in this way, as also subsequently, on removing the barium or strontium and calcium ions from the solution with ammonium carbonate: These precipitates may retain ions of the alkali metals, owing to adsorption. They must, therefore, be well washed, as otherwise there is a danger of small quantities of potassium and sodium ion being overlooked.

The separation of barium and calcium ion is never complete, particularly if the ammonium carbonate precipitate is well washed. Such separation must, therefore, be repeated in the filtrate, after the renewed expulsion of ammonium salts, and if any appreciable precipitate is then produced, it is necessary to repeat this until the solution remains quite clear on the addition of ammonium carbonate. Only after the ammonium salts have been finally expelled are tests applied as in (171). The second or third ammonium carbonate precipitate is not washed for too long a time, because, otherwise, ions of the alkaline earths are always re-dissolved.

70. In testing for potassium ion (171), it is necessary to guard against errors due to a small residue of unvolatilised ammonium salts. This residue frequently sublimes at the upper edge of the dish. It must also be expelled from there, by heating, before the contents of the dish are dissolved in water.

If a doubt exists as to whether the solution under examination is actually free from ammonium salts, a portion should be tested for ammonium ion as in (172). (The solution must be protected from the ammonia vapours in the laboratory air.)

The best method of detecting very small quantities of potassium ion in testing according to (171, *a*) is to evaporate the liquid to dryness, and to take up the residue with *dilute* alcohol.

In testing solutions containing iodine ion by means of platinohydrochloric acid, a dark red coloration appears, owing to platino-iodide ion and iodine (Sec. 31, 2 ; Sec. 85, 8), whereby the yellow precipitate of potassium platinochloride is easily masked. (On looking at the clock-glass from underneath, however, it may easily be recognised.) In this case, it is preferable to make the test according to (171, β).

What might be mentioned here with regard to the detection of lithium, cæsium, and rubidium ions has already been said on pp. 132, 134, and 136, and also in connection with the analysis of mineral waters (258) and (259). **71.**

Notes to Secs. 158 *and* 175.

The precipitation of the anions of the first group by means of barium ion in the manner described in (175) is influenced by the presence of salts (chlorides, nitrates) of ammonium and the alkali metals, and, to a greater degree, the more weakly negative the anions are, or the weaker the acids with which they correspond. Consequently on the addition of barium chloride, the solubility product of the barium salts of the first and third division of the first group of anions is not reached, and no precipitation takes place (175). This applies especially to borate ion, in the case of which the same conditions occur in regard to precipitation with silver nitrate (176). It also applies to the calcium salts of organic acids, especially those of citric, malic, and succinic acids, which are not precipitated by calcium chloride in the presence of ammonium chloride. **72.**

In the detection of iodine ion (178), it is stated that the iodine should first be liberated with nitrous acid, and only then chlorine water added. The reason for this is that on the direct addition of chlorine water to the liquid which is being tested for iodine ion, small amounts of iodine may be overlooked, if only sufficient chlorine water is added to convert the iodine, which is first liberated, immediately into colourless iodine chloride (Sec. 119, 11). **73.**

In the event of chlorine being present simultaneously with iodine, disturbing by-reactions may, under certain conditions, occur on the addition of potassium nitrite and sulphuric acid, or nitrous acid and sulphuric acid. If this is presumed to be the case, ferric chloride may also be used for the liberation of the iodine.

If iodine ion was found, it is recommended that chlorine water should be added until decolorisation occurs, in order that a test for bromine ion may be made by the addition of more chlorine water. In the presence of much iodine ion this requires a large quantity of chlorine water, and there is a danger of finally adding so much that the excess causes the liberated bromine to be oxidised again to a colourless compound (Sec. 118, 6).

It is advisable, therefore, in the presence of much iodine ion, to add at first only sufficient chlorine water to colour the carbon bisulphide dark violet, then to filter it through a moistened filter, to add a little more carbon bisulphide to the filtrate, and then, carefully, more chlorine water. If this also produces a deep violet coloration, the carbon bisulphide may be separated and the test repeated. In any case, the liquid must be *well* shaken after each addition of chlorine water.

74. The direction is given in (179) that only 1 to 2 drops of ferric chloride solution should be added. The reason for this is that iodine may be liberated by the addition of ferric chloride in the presence of iodine ion. If present in large quantity it may form a *red* solution, owing to the presence of undecomposed iodide, so that it may be mistaken for thiocyanate ion. If only a few drops of ferric solution are added, however, *no red coloration* is obtained in the absence of thiocyanate ion (at most a *yellow* coloration, due to the iodine).

75. It is stated in (182, 8) that a preliminary test should be made for oxalate or fluorine ion by means of calcium chloride and the subsequent addition of acetic acid, and that, although only the non-appearance of a permanent precipitate indicates the absence of both anions, the formation of a precipitate does not justify the conclusion that one of these two anions must be present. For instance, such a precipitate may be due to silicate ion, in very concentrated solutions also to sulphate ion; further, if acetic acid was not added at once, also to phosphate ion; and finally, if organic acids are present, to cinnamylate or tartrate ion.

Notes to Sec. 175 (175).

76. If, in an analysis silicofluoride ion is to be taken into consideration, it should be noted that the precipitate formed in (175, *b*) may contain barium silicofluoride. A microscopical test for it is therefore made under a magnification of 140–200 diameters, a portion of the precipitate being examined, first as it is, and then after the addition of a drop of dilute hydrochloric acid, which dissolves any barium phosphate, barium oxalate, etc., present. The characteristic crystals of barium silicofluoride may often be detected before, but more readily after, this treatment with hydrochloric acid.

For the chemical detection of barium silicofluoride, a portion of the precipitate left after the careful addition of hydrochloric acid or nitric acid (barium silicofluoride is somewhat soluble in acids) may then be heated with sulphuric acid, as in Sec. 111, 7, in a current of air.

If barium silicofluoride is detected in the barium salt precipitate insoluble in hydrochloric or nitric acid, another sample of the precipitate must be tested for sulphate ion. This is done by igniting the sample, triturating the residue, and heating it with hydrochloric acid of sp. gr. 1·12. The barium fluoride resulting from the ignition of the barium silicofluoride then dissolves, whilst any barium sulphate present is left, and may then be further examined as in Sec. 105, 9.

Notes to Secs. 159, 162, 176, *and* 178.

In the first place, it should be specially noted in the practical **77.** examination of unknown substances that the course only applies to the organic acids or anions dealt with in this book, which generally occur in nature and more or less frequently in daily life; it must therefore naturally fail when other (*e.g.* synthetically prepared) compounds are under consideration. Reference may again be made here to what was said in No. 3 of this chapter. It is assumed in the course described in Secs. 159, 162, 176, and 178, that apart from the precipitation of cinnamic acid (benzoic acid and salicylic acid) by means of hydrochloric acid, free acids or alkali salts are present. If these have first to be separated in the presence of other cations, care should be taken that no disturbing substances remain in the solution under examination. Thus, above all, no carbonate ion should be present after treatment with sodium carbonate solution (78), (97), (185), (198), as this produces a precipitate in the subsequent test with calcium chloride, and renders a test necessary for the members of the first group of organic anions, even when they are not there at all; further, a calcium carbonate precipitate renders the test for these anions more difficult, because their calcium salts can be less readily detected in the presence of much calcium carbonate. Especial care, therefore, should be taken in removing the carbon dioxide after acidification (79), (97), (185), and (198). If it is removed by boiling, however, volatile organic acids may also escape detection, so that acetate ion and formate ion may not be recognised. The liquid is therefore not heated to boiling point, but the warm solution vigorously and continuously shaken.

The last remark naturally applies also to the removal of hydrogen sulphide.

Further, it should be noted that when inorganic anions of the first group are present, they also may yield precipitates in the test with calcium chloride, so that the formation of a precipitate in (185, 2) does not justify the conclusion that a member of the first group of organic anions *must* be present.

78. The separation of cinnamic acid, benzoic acid, and salicylic acid by means of hydrochloric acid takes place in the presence of cations of Group V_1, simultaneously with their chlorides, and from alkaline solutions possibly simultaneously with silicic acid, sulphur, and sulphides. In exceptional cases, boric acid may also be precipitated from concentrated solutions. The separation of these organic substances (apart from boric acid) should be effected by shaking with ether.

The simplest way of separating the ether phase from the aqueous phase is by means of a small apparatus similar to a washing bottle, the longer tube of which is immersed in the ethereal layer to just above the plane of separation. If boric acid is present, it may, in certain cases, also pass into the ethereal solution.

79. The test which is made to determine whether the precipitate obtained by means of calcium chloride in (185) dissolves in sodium hydroxide solution must be carried out with sodium hydroxide free from carbonate, since otherwise calcium carbonate separates and correspondingly less calcium ion dissolves, so that, on boiling, no precipitate of calcium tartrate may be formed.

80. If a precipitate was formed in (185), the filtrate frequently no longer contains so much calcium ion that when three parts of alcohol have been added in (187) the solubility product is exceeded; the addition of a little more calcium chloride is therefore advisable. Since the liquid must stand for a few hours, the tube should be corked, as otherwise a precipitate of calcium carbonate may be formed, owing to the absorption of carbon dioxide from the air, and may be confused with citrate, malate, or succinate.

81. It is stated in (188, *c*) that the calcium precipitate should be completely freed from alcohol by drying before treatment with nitric acid. The reason for this is that oxalic acid may also be formed from alcohol on heating with nitric acid. The detection of oxalate ion after treatment with nitric acid is consequently only a proof of the original presence of malate ion when alcohol no longer adheres to the precipitate.

82. General rules cannot be given for the possibility of anions of rarer occurrence being present, especially in the presence of those of more frequent occurrence. In this respect reference should be made to the "*Summary and Remarks*" at the end of the third group of inorganic anions, the end of Sec. 132, and also to Secs. 148 and 149, 10.

With reference to the detection of the anions of inorganic compounds insoluble in water but soluble in acids, it is stated in (194) that the insoluble substance (if necessary extracted with water) should be fused with sodium carbonate, and the anions detected in the aqueous solution of the fused mass. If the portion insoluble in water is only partly soluble in acid, care should be taken that the anions of the compounds insoluble in acid are also present in the aqueous solution of the fused mass. It must, therefore, be borne in mind in this case that not all the anions which are found originate in the portions soluble in acid, and that those found subsequently in Sec. 179 are not included here.

Notes to Sec. 179.

Directions have been given in the course for substances insoluble in acids that, before fusing them in a platinum crucible, lead and silver compounds should be removed. Tests for these substances are made simultaneously in the solutions thus obtained. Ammonium acetate solution should be used to dissolve the lead compounds. It should be slightly *acid;* if it were ammoniacal it could also dissolve silver compounds, which might then entirely escape detection. The ammonium acetate solution should be concentrated. It is allowed to act repeatedly on the substance in a small flask, decanted through a filter, and the filtrate tested with hydrogen sulphide. The lead must be *completely* removed, as otherwise the platinum crucible will be damaged in the subsequent fusion. **83.**

In testing the ammonium acetate solution for chlorine ion, the direction is given in (205) that it should be diluted with 20 parts of water before the addition of silver nitrate solution. The reason for this is that otherwise a precipitate might be formed, even in the absence of chlorine ion, since silver acetate is only sparingly soluble.

In removing the silver salts with potassium cyanide the treatment should be continued until the salts are completely extracted, to avoid damaging the platinum crucible. The filtrate is tested by acidification with nitric acid. In this operation hydrocyanic acid is evolved, for which reason great *care* should be taken and the acidification effected in a fume cupboard. **84.**

If silver compounds are found in the residue insoluble in hydrochloric acid, it is not a proof that the original substance also contained insoluble silver compounds, as, on the one hand, silver chloride may have been formed in the treatment with hydrochloric acid or *aqua regia*, and, on the other, insoluble silver compounds may result from the simple treatment with water of a mixture of substances soluble in water, *e.g.* in the simultaneous presence of mercuric iodide and silver nitrate. Insoluble silver compounds originally present, however, may, under certain conditions, react with other substances in such a way that the residue under examination in Sec. 179 may contain other compounds than the original mixture. For example, silver chloride and potassium iodide interact, on treatment with water, to form silver iodide and potassium chloride.

It is, therefore, only conditionally possible to determine by means of purely qualitative analysis the form of combination in which silver, found in the insoluble residue, was present in the original substance.[1]

85. At the end of (208) it is said that the washing should be continued until barium chloride no longer produces a precipitate with the washings. If this is neglected, that is to say, if the residue from the fusion insoluble in water still contains portions of the anions, the compounds present before decomposition are formed again on dissolving the residue from the fusion in hydrochloric acid. For instance, on solution in hydrochloric acid, barium sulphate is formed again from barium carbonate to which sodium sulphate still adheres.

86. It is stated in (211) that the hydrochloric acid solution of the residue insoluble in water should be tested for cations. It should be noted that only *those* cations have to be taken into consideration which form compounds insoluble in acids with the anions detected, or which may occur in the substances mentioned at the beginning of Sec. 179.

Consequently, in so far as it is not a question of silicates, practically only the ions of tin, aluminium, and the alkaline earth metals enter into consideration here.

87. In order not to complicate the course, no attention has been paid in Secs. 170, 177, and 179 to the possible necessity of detecting small quantities of silicic acid in the presence of large quantities of calcium fluoride or another fluoride. Should this necessity occur, as is not infrequently the case in the analysis of fluorine minerals, it is possible to overlook the silicic acid when proceeding as described in (183, 10) and (196) or (210), because the silicon in it may volatilise completely as silicon fluoride on evaporating the alkaline solution of the fused mass with hydrochloric acid (p. 634, footnote 1). In order to separate silicic acid in (208) when analysing substances which contain fluorine, either the alkaline solution of the fused mass prepared as in (194) must be heated with ammonium carbonate (the volatilising ammonium carbonate being replaced), and filtered, and the filtrate treated with an ammoniacal solution of zinc hydroxide (prepared by treating a zinc salt solution with sodium hydroxide, washing the zinc hydroxide and dissolving it in ammonia solution), in order to separate the remainder of the silicic acid, then evaporated until all the ammonia has escaped, and filtered. Silicon dioxide is then liberated from the precipitate formed by ammonium carbonate, by evaporation with hydrochloric acid, but in the case of the precipitate formed in the ammoniacal zinc solution evaporation with nitric acid is preferable. An alternative method is that of Seemann (*Zeitsch. anal. Chem.*, **44**, 364), in which the alkaline solution containing silicic acid and fluorine ion is neutralised with hydrochloric acid (an indicator being used), a solution of precipitated washed mercuric oxide in ammonium carbonate solution which has been treated with ammonia[1] added, the mixture evaporated to dryness, the residue taken up with water and filtered; the residue contains the silicic acid in the form of a mercury compound. On ignition pure silicon dioxide is left.

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[1] The same applies, of course, in many other cases. For example, in the analysis of a mixture of sodium sulphate and barium chloride, insoluble barium sulphate is formed, and in that of a mixture of ammonium fluoride and calcium nitrate, insoluble calcium fluoride.

88. If, in Sec. 179, the elements of less frequent occurrence are taken into consideration, the number of substances which can be left undissolved on treatment of the substance under examination with water, hydrochloric acid, nitric acid, and *aqua regia* is considerably increased. In particular, the following elements and anions are those which, partly in the ignited condition or in certain compounds, have proved to be insoluble in acids, or to dissolve slowly and with difficulty therein: Beryllium, thorium and zirconium, cerium, titanate ion, tantalate ion, niobate ion, molybdate ion, and tungstate ion, rhodium, iridium, osmium and ruthenium.

When the point (208) has been reached in the course of analysis, the substance, free from silver, lead, and sulphur, is fused with sodium carbonate and a little potassium nitrate, the mass extracted repeatedly with water, any residue still undissolved fused in a silver crucible with potassium hydroxide and potassium nitrate (*cf.* Sec. 15, p. 59, footnote 1), and again treated with water. The alkaline solutions, which may be combined or examined separately, may contain beryllium, a portion of the titanium, tantalum, niobium, molybdenum, and tungsten, osmium, ruthenium, and a portion of any iridium present.

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[1] Schaffgot's solution: 235 grms. of ammonium carbonate and 180 c.c. of 25 per cent. ammonia solution dissolved in 1 litre. To this solution is added in the cold, so long as anything still dissolves, freshly precipitated mercuric oxide, obtained by treating a mercuric chloride solution with potassium or sodium hydroxide, and carefully washing the precipitate.

If the residue which remained insoluble in the previous operations is fused with potassium hydrogen sulphate, thorium, zirconium, cerium, the remainder of the titanium and the rhodium will dissolve on treating the fused mass with water.

If a residue was still left it might be due to platinum metals which were not decomposed, and should preferably be mixed with sodium chloride and ignited in a current of chlorine.

So far as the separation and differentiation of the individual elements in the different solutions is concerned, all that is necessary has been said in the notes to Secs. 164 to 175, and also in Chapter III., of Part I.

IV. Other Systematic Courses of Qualitative Analysis.

As was emphasised on p. 544, on the one hand the sequence of reactions employed for the separation and detection of individual substances may naturally be arranged in various ways, and on the other, reactions may be employed for the systematic separation of substances into groups, or for their individual detection, which differ entirely from those upon which the systematic course described in Secs. 150 to 179 is based.

From time to time, therefore, numerous suggestions for other suitable methods of separation and detection have been made. Many of them, in so far as they are concerned only with the differentiation of substances of similar behaviour (members of the different groups as classified in this book), have been mentioned in the respective "*Summary and Remarks*," and may, therefore, be used in the corresponding parts of the course instead of the directions given above, though the main principles of separation should be followed.[1] Others, however, employ reactions based on totally different principles for separating the elements into main groups, the most important of which will now be briefly described.

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[1] A new method of separating the filtrate from the hydrogen sulphide precipitate has been devised by H. Remy (*Zeitsch. anal. Chem.*, **58**, 385).

A. Methods of separation for cations.

All the following processes are based on the same principle, *i.e.* the avoidance of hydrogen sulphide, which, in many ways, is disadvantageous and objectionable, as has been found by different people in a varying degree.[1]

Some of these processes include precipitation with sulphide, and are therefore more or less related in their main points to the systematic course described above ; others, however, include few, if any, sulphide precipitations, and consequently involve a considerable deviation in the grouping of cations.

1. Schiff and Tarugi's Thioacetate Method.[2]

In this method the hydrogen sulphide is replaced by thioacetic acid, which is made to react by adding a slightly ammoniacal solution of ammonium thioacetate to the hydrochloric acid solution containing the remaining cations (or to that filtered from the silver, mercurous, or lead chloride precipitate) The liquid is heated (whereby all the precipitates which separate at first, and some of which are of a different colour and composition, are converted into sulphides) and then allowed to cool, when the cadmium sulphide, which at first dissolved, separates again.

Otherwise, the ordinary course is followed. The ammonium thioacetate solution is decomposed by hydrochloric acid, with the formation of very active hydrogen sulphide and acetic acid :

$$CH_3.COS'+H^{\cdot}+H_2O=H_2S+CH_3.COOH$$

Thioacetic acid is prepared by the action of glacial acetic acid on phosphorus pentasulphide. As the reagent has an unpleasant odour, and is difficult to obtain and somewhat expensive, the thioacetate method has not been generally adopted.

2. Vortmann's Sodium Sulphide Method.[3]

(*a*) The substance present in the nitric acid or hydrochloric acid solution is *oxidised with bromine water* or by heating it with *potassium chlorate*, solid sodium carbonate added until effervescence ceases, and the mixture rendered alkaline with sodium hydroxide and heated.

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[1] A comprehensive treatment of this question is to be found in Ed. Donath's *Über den Ersatz des Schwefelwasserstoffs in der qualitativen chemischen Analyse.* Leipzig, published by S. Hirzel, 1909.

[2] *Ber.*, **27**, 3437 ; *Zeitsch. anal. Chem.*, **34**, 456.

[3] Georg Vortmann, *Allgemeiner Gang der qualitativen chemischen Analyse ohne Anwendung von Schwefelwasserstoff.* Vienna, Franz Deuticke, 1908.

If *ammonium ion* is present, ammonia escapes. Sodium sulphide (which should be free from sulphate) is added in excess, and the mixture heated and filtered.[1] The precipitate is dealt with as in (*e*), and the filtrate as in (*b*).

(*b*) The *filtrate* from (*a*), which may contain aluminate ion, as also the ions of the sulpho-salts of arsenic, antimony, tin, mercury, and nickel, is treated with solid *ammonium chloride* and *heated*. The precipitate is dealt with as in (*d*), and the filtrate as in (*c*).

(*c*) *The filtrate from* (*b*) *is treated with hydrochloric acid.* The sulphides of arsenic, antimony, and tin separate.[2] The separated precipitate is boiled with hydrochloric acid, which leaves the arsenic sulphide undissolved; this residue is then dissolved in nitric acid. The presence of *arsenate ion* in the solution is confirmed by treatment with magnesium chloride and ammonia or silver nitrate. The *antimony* is separated in the form of a black powder by means of iron wire from the filtrate from the arsenic sulphide; confirmation is obtained by dissolving it in tartaric acid and nitric acid, and treating the solution with sodium sulphide (an orange-red precipitate should be formed) *Tin ion* is detected, by means of mercuric chloride, in the filtrate which was freed from antimony by iron: a *white* precipitate of Hg_2Cl_2 or a grey one of Hg is formed.

(*d*) The *precipitate*[3] produced by ammonium chloride in (*b*) is *heated with dilute sulphuric acid.* The filtrate is treated with ammonia, to precipitate any *aluminium ion* present (white precipitate). The residue is boiled with dilute nitric acid, and the filtrate tested for *nickel ion* by means of bromine and ammonia (a brownish-black precipitate of $Ni(OH)_3$ is formed). The residue is dissolved in a little *aqua regia,* and *mercuric ion* detected by means of stannous chloride (the precipitate is white or grey).

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[1] The precipitate is washed with sodium sulphide solution. If nickel ion is present (which is generally indicated by the brown colour of the filtrate) sodium sulphite is added to the washing liquid, by which means the precipitate may be obtained quite free from nickel. The washing liquid is not added to the filtrate.

[2] In the presence of organic substances the filtrate may still contain aluminium ion, for which it is tested by treatment with ammonia in excess and the addition of sodium phosphate.

[3] It is only free from arsenic, antimony, and tin if these were present in the highest state of valency. For this reason the substance is oxidised in (*a*).

(*e*) The *precipitate* from (*a*), which, in addition to the sulphides of the heavy metals, contains the carbonates and possibly the phosphates of the alkaline earth metals, as also chromic hydroxide, is *treated in the cold with dilute hydrochloric acid* which has been saturated with hydrogen sulphide by introducing sodium sulphide solution into the bottom of the flask. The still insoluble residue is treated as in (*i*), and the filtrate as in (*f*).

(*f*) *The hydrochloric acid solution of the sodium sulphide precipitate* from (*e*), which may contain the ions of magnesium, calcium, strontium, barium, chromium, uranium, iron, zinc, manganese (and small quantities of cobalt and nickel ion), and also phosphate ion, is treated, after expulsion of the hydrogen sulphide and cooling, with *solid sodium carbonate in excess and bromine, and then heated.* The precipitate is dealt with as in (*h*), and the filtrate as in (*g*).

(*g*) The solution obtained in (*f*) may contain chromium (as chromate ion), manganese (as permanganate ion), and uranium (as uranate ion).

If the *solution is red, it is heated with a little alcohol,* whereupon the *manganese* separates as hydrated dioxide. A yellow coloration appearing directly, or after precipitation of the manganese, indicates *chromate ion.* As a confirmatory test, the liquid is acidified with acetic acid and treated with lead acetate.

After acidification with acetic acid, a test is applied for uranate ion by means of potassium ferrocyanide.

(*h*) The precipitate produced by sodium carbonate and bromine in the hydrochloric acid solution of the sodium sulphide precipitate in (*f*) contains the carbonates or phosphates of the alkaline earth metals and of zinc, and also iron in the form of hydroxide or phosphate, and manganese as hydrated dioxide. *A small portion is dissolved in nitric acid,* and the liquid tested with ammonium molybdate solution for *phosphate ion. The main precipitate is dissolved in hydrochloric acid* (in the presence of phosphate ion a small portion is tested with potassium ferrocyanide for *ferric ion,* and, irrespective of whether it is found or not, ferric chloride added) until, on treating a small quantity of the solution with ammonia, a *brown* precipitate is produced.

The hydrochloric acid solution is almost neutralised with sodium carbonate, treated with sodium acetate, and boiled. *Ferric ion* is precipitated as basic acetate, any phosphate ion present passing into the precipitate. If *manganous ion* is present, bromine water and ammonia produce a brown precipitate in the filtrate when heated. The precipitate is filtered off, and the filtrate treated with ammonium carbonate. The precipitate of barium, strontium, and calcium carbonates is tested for these three substances by the known methods. The filtrate from the carbonates still contains *zinc and magnesium ions*. The former is precipitated by means of sodium sulphide,[1] and the latter separated in the filtrate from this by means of sodium phosphate.

(*i*) The *residue* from (*c*), *insoluble* in hydrochloric acid saturated with hydrogen sulphide, is boiled, after washing, with dilute *nitric acid*. The residue is dealt with as in (*l*), and the solution as in (*k*).

(*k*) The *solution* from (*i*) is treated with *hydrochloric acid* in order to precipitate *silver ion*; the *filtrate* from the silver chloride is *evaporated with sulphuric acid* for the purpose of separating the *lead ion* as sulphate. The filtrate is rendered *ammoniacal*; a white precipitate points to *bismuth ion* (confirmation being obtained by dissolving it in a little acid and diluting it with water); a blue coloration indicates *copper ion*. The copper, cadmium, and cobalt ions are precipitated by means of a little sodium sulphide, and the sulphide precipitate boiled with sulphuric acid. *Cadmium sulphide* dissolves, and may be precipitated, after neutralisation, with sodium sulphide. *Copper ion* is precipitated by means of potassium thiocyanate and sulphur dioxide from the nitric acid solution of the residue which

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[1] If, on treating the first sodium sulphide precipitate, the hydrochloric acid did not contain sufficient hydrogen sulphide, the precipitate may contain cadmium. Small quantities of cobalt and nickel may also frequently be present in it. If, therefore it is not quite white, the precipitate is dissolved in nitric acid, the solution treated with sodium hydroxide and a little bromine water, and the filtrate tested for zinc ion by means of sodium sulphide. The precipitate produced by sodium hydroxide and bromine is dissolved in hydrochloric acid, the solution rendered ammoniacal after the hydrogen sulphide has been expelled, and potassium cyanide and sodium sulphide added. A yellow precipitate indicates *cadmium sulphide*.

was not dissolved by sulphuric acid; *cobalt ion* is p
cipitated from the filtrate by bromine and sodium hydroxi
Since a precipitate may still contain portions of nickel, t
presence of cobalt must be confirmed by a borax bead te

(*l*) The insoluble residue left in (*i*) may, in addition to sulph
still contain black mercuric sulphide or its white doub
salt: $2HgS,Hg(NO_3)_2$, silver sulphide and lead sulphate

It is tested for *lead ion* by extraction with ammoniu
acetate and treatment of the filtrate with potassiu
dichromate; the residue is examined for *mercuric ion* l
treatment with *aqua regia* and addition of stannous chlori
to the filtrate; finally, the residue, insoluble in *aqua reg*
is tested for *silver ion* by extraction with ammonia soluti
and acidification with nitric acid.

(*m*) *Alkali ions* may be detected in the original solution,
other cations are not present, by the method described
p. 579. If other cations are present, the examination
made as on p. 650.

3. Vortmann's Thiosulphate Method.[1]

(*a*) Silver ion, mercury ion, and a portion of the lead ion a
precipitated with hydrochloric acid, and the precipitate treat
as on p. 603.

(*b*) The sulphates of lead, barium, strontium (and calcium) a
precipitated with sulphuric acid. The filtrate is dealt wit
as in (*c*). The *precipitate is boiled* with strong *sodiu*
carbonate solution, and the washed precipitate treated wit
acetic acid; the carbonates of lead, strontium, and calciu
(together with small quantities of barium) dissolve. *Bariu*
sulphate remains undissolved.

Lead ion and the remainder of the barium ion a
separated by means of potassium chromate from the *acet*
acid solution. After filtration the liquid is neutralise
with ammonia, and *heated*, after the addition of a fourth
its volume of *alcohol*. *Strontium* chromate is precipitate
If a white precipitate is produced in the filtrate by *ammoniu*
oxalate, the presence of *calcium ion* is indicated.

(*c*) A small portion of the *filtrate* obtained in (*b*) is tested b
boiling it with *sodium thiosulphate*, to see whether a coloure

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[1] *Monatsh.*, 1868, p. 418.

or a white pulverulent precipitate is formed, or whether only a separation of sulphur (possibly in the form of fused drops) is produced.

If a precipitate is formed, the whole of the liquid intended for the precipitation of cations is treated with *sodium thiosulphate*, while the following points, already mentioned by Orlowski,[1] must be noted. 1. The reaction of the liquid must be very slightly acid throughout the test. 2. It should contain little, if any, free nitric acid. 3. The sodium thiosulphate should be added in small quantities, and, after each addition, the liquid well mixed, boiled for two to three minutes, allowed to stand, and the supernatant liquid tested to see whether a precipitate has been formed, or whether it is still acid.

(*d*) *The precipitate is treated with ammonium sulphide, and the liquid filtered.* The solution, which contains *arsenic, antimony*, and *tin* as sulpho-anions, is acidified in order to precipitate the sulphides, and these then separated in the usual way (see p. 617). The residue, insoluble in ammonium sulphide, contains, in addition to the sulphides of mercury, bismuth, copper, and cadmium, more or less aluminium, chromium, and uranium as *hydroxides*.

It is boiled with dilute nitric acid, whereby *mercury* is left as sulphide, and the filtrate treated with sodium hydroxide in excess, then with sodium hypochlorite, and boiled. *Aluminium hydroxide* dissolves as aluminate ion, and may be precipitated by boiling with ammonium chloride; *chromium hydroxide* dissolves as chromate ion, which may be recognised by its yellow colour, and which is precipitable in acetic acid solution with lead acetate. The residue is dissolved in hydrochloric acid and treated with ammonia, whereby complex *copper and cadmium ions* remain dissolved, and may be separated in the usual way. The residue, which may contain bismuth and uranium, is re-dissolved in hydrochloric acid and treated with ammonium carbonate and ammonia in excess; *bismuth ion* separates, while *uranyl carbonate* remains in solution, and may then be precipitated by means of acetic acid and potassium ferrocyanide.

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[1] Orlowski first suggested a systematic course of qualitative analysis by means of alkali thiosulphate (*Zeitsch. anal. Chem.*, 22, 357). On page 360 of that communication a statement is made which must be due to an error, because at the beginning of the course lead, barium, and strontium ions should surely be precipitated with sulphuric acid or an alkali sulphate.

(*e*) The *filtrate* obtained in the thiosulphate precipitation in (*c*) is treated as in the ordinary way with *ammonia and ammonium sulphide*, after the addition of ammonium chloride. The precipitate is separated as usual. It may also contain cadmium, which may be found with nickel and cobalt and sometimes with zinc. With regard to its detection in the presence of these metals, see Vortmann's sodium sulphide method, (*h*), footnote on p. 840.

(*f*) Tests for *calcium ion* (which was at most incompletely precipitated in (*b*)) must be made by means of *ammonium oxalate* in the *filtrate* from the *ammonium sulphide precipitate*, and the filtrate from this tested for *magnesium ion* with sodium ammonium hydrogen phosphate. A separate portion is tested for alkali ions (see Vortmann's sodium sulphide method, (*m*), p. 841), and another sample must be tested as usual for *ammonium ion* by means of calcium hydroxide.

4. Ebler and Knoevenagel (and Ebler's) Method of Separation by means of Hydrazine and Hydroxylamine Salts.[1]

(*a*) The substance, if soluble in water or nitric acid, is *evaporated* (if necessary repeatedly) *with concentrated nitric acid* until it is free from chloride. This is done without other treatment if the substance is soluble in water or nitric acid, but otherwise after it has been dissolved in *aqua regia* (and any residue insoluble therein filtered off and tested by itself as usual, see p. 671). Tin and antimony separate as oxides; the residue is well washed with dilute nitric acid and water, and fused with a mixture of potassium carbonate and sulphur. The fused mass is dissolved in water (if any residue is left which may contain copper, lead, bismuth, etc., as sulphides, it is dissolved in nitric acid, and the solution added to the main filtrate) and treated with sulphuric acid. The sulphides which are precipitated are separated in the ordinary way.

(*b*) The *filtrate* is tested in the cold with *ammonium molybdate* for *phosphate ion*, and eventually, after filtering off the precipitate, by heating, for *arsenate ion*. If phosphate ion was present, it should be removed by heating the liquid with granulated tin on the water bath.

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[1] Adapted from the above-mentioned communication of Donath.

(*c*) The *solution*, free from phosphate, is *heated with an excess of hydrochloric acid* to separate *silver ion*. Any silver chloride precipitate formed is washed with hot dilute nitric acid.

(*d*) If arsenate was present, the solution, free from phosphate and silver ions, is treated with *hydrazine chloride* and *fuming hydriodic acid* to reduce the arsenate ion to arsenite ion, and hydrazine chloride added little by little until the liquid remains colourless.[1]

(*e*) The *main solution* (possibly treated as in (*b*) to (*d*) [2]) which, if hydriodic acid was added in (*d*), may be rendered turbid by insoluble cuprous, mercurous, etc., iodide, is treated with 10 c.c. of a solution of hydroxylamine hydrochloride (1 : 5), then with concentrated ammonia solution in excess, heated on the water bath until the liquid no longer has the odour of ammonia, filtered, and thoroughly washed with hot water. The precipitate is treated as in (*f*), and the filtrate as in (*m*).

(*f*) The *precipitate* from (*e*) contains aluminium, chromic, ferric, bismuth, and lead hydroxides and metallic mercury. It is dissolved by heating it with *concentrated nitric acid*, and the solution *treated with ammonia*. The *mercury* remains in solution as complex mercuric ammonium ion, and is separated as metal from the filtrate by means of 5 c.c. of hydroxylamine (1 : 5), the liquid being meanwhile heated for half an hour on the water bath. The ions of the remaining metals are precipitated as hydroxides.

(*g*) The *hydroxide precipitate* obtained in (*f*) is *dissolved in dilute hydrochloric acid*, and the solution evaporated to dryness several times on the water bath to expel all the free acid, the residue taken up with *hot water*, and the solution filtered. The residue is *bismuthyl chloride*.

(*h*) *Lead ion* is precipitated with sulphuric acid from the filtrate from (*g*).

(*i*) The filtrate from (*h*) is poured into a mixture of equal parts of 20 per cent. sodium hydroxide solution and 3 to 4 per cent. hydrogen peroxide solution.[1] *Ferric hydroxide* is precipitated.

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[1] The reduction of arsenate takes place in accordance with the equation: $AsO'''_4+4H^{\cdot}+2I' \rightleftarrows AsO'_2+2H_2O+2I$, and only proceeds quantitatively from left to right if the free iodine has been expelled (by hydrazine): $4I+N_2H_4=N_2+4H^{\cdot}+4I'$.

[2] Instead of reducing the arsenate with hydriodic acid, it may be removed by distillation with methyl alcohol, with the introduction of gaseous hydrochloric acid. This is particularly advisable in the presence of borate ion.

(*k*) The filtrate from (*i*) contains aluminate and chromate ions, the latter being recognisable by its yellow coloration. It is boiled with an excess of ammonium chloride until the odour of ammonia has disappeared. The formation of a precipitate indicates *aluminium hydroxide.*

(*l*) The *filtrate* from (*k*) is acidified with *hydrochloric acid* and boiled with *hydroxylamine chloride;* chromate ion is reduced to chromic ion (the colour changes from yellow to green). Ammonia precipitates chromic hydroxide.

(*m*) The filtrate[2] from the first ammonia precipitate (*e*) is *acidified* with *hydrochloric acid* and (if iodine ion is not already present, owing to the reduction of arsenate) a little *ammonium thiocyanate* is added. *Cuprous* iodide or thiocyanate is precipitated, and the solution is heated until the precipitate has subsided, leaving a clear liquid. The precipitate is then tested for copper, and the filtrate treated as in (*n*).

(*n*) The *filtrate* (which is decolorised by heating with a little hydrazine chloride if it is of a yellowish colour owing to iodine) is rendered *ammoniacal,* heated to boiling point, and treated with *ammonium sulphide.* The precipitate is treated as in (*o*), and the filtrate as in (*s*).

(*o*) The washed *precipitate* from (*n*) is dissolved in as little concentrated *hydrochloric acid* as possible, if necessary after the addition of a little nitric acid, the solution evaporated on the water bath, the residue taken up with a little water, and *the solution introduced into a sodium hydroxide solution containing hydrogen peroxide* (see (*i*)), heated for half an hour on the water bath, and filtered. The precipitate is dealt with as in (*p*). The filtrate, which contains *zincate ion,* is treated with a little ammonium sulphide; white *zinc sulphide* is precipitated.

(*p*) The *precipitate* from (*o*) is *dissolved in hydrochloric acid,* the solution boiled until the chlorine, resulting from the solution of manganese dioxide or cobaltic and nickelic hydroxides, has been removed, then poured into a *strongly* ammoniacal hydrogen peroxide solution, heated for a quarter of an hour in a covered vessel, and filtered. The precipitate is hydrated manganese dioxide. The filtrate is treated as in (*q*).

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[1] Potassium percarbonate may be used instead.

[2] If it has a bluish colour, owing to the influence of the air, it is heated with a few drops of hydrazine or hydroxylamine chloride, in order to convert the cupric ion into the monovalent form again.

(*q*) The *filtrate* from (*p*) is *concentrated by boiling*, treated with *fuming nitric acid*, evaporated to dryness, and heated to about 250°, so that the greater portion of the ammonium salts is removed. The residue is dissolved in as little hydrochloric acid as possible and a portion tested for *cobalt ion* with *potassium nitrite*, after the addition of sodium acetate. The remainder is treated with *potassium cyanide* and a little sodium hydroxide, gently heated, and *ammonium sulphide* added. *Cadmium sulphide* separates as a yellow precipitate. The filtrate is dealt with as in (*r*).

(*r*) The *filtrate* from (*q*) is *boiled* in the air to oxidise the potassium cobaltocyanide to potassium cobalticyanide, and then treated with *bromine* and *sodium hydroxide*. *Nickel ion* is precipitated as black nickelic hydroxide. Cobalt ion may be precipitated from this filtrate, after evaporation with sulphuric acid, by treatment of the aqueous solution with sodium hydroxide, and may be identified in the usual way.

(*s*) *The filtrate of the ammonium sulphide precipitate* in (*n*) contains *arsenic* (if it has not been removed by distillation) in the form of a sulpho-salt ion; this may be *precipitated* in admixture with sulphur by *acidifying the liquid with hydrochloric acid and boiling it.* It is evaporated with nitric acid, the residue dissolved in water, and arsenate ion identified in the solution by means of magnesia mixture.

(*t*) The filtrate separated from the precipitated sulphur (possibly containing arsenic) contains the ions of the alkaline earths and alkalis, which, after the ammonium salts have been removed, may be separated and identified in the ordinary manner.

5. Gustav Almkvist's Method of Separation, based on the Different Precipitability with Potassium Hydroxide and Potassium Carbonate.[1]

(*a*) The substance is dissolved in acid (in *aqua regia*, if iodine or cyanogen ion is present), evaporated to a small residue, and this treated with potassium hydroxide. The solution is boiled until all the *ammonia* has escaped, treated with potassium carbonate and hydrogen peroxide, again boiled for 10 minutes, and filtered. The precipitate is treated as in (*g*). The solution, which contains the ions of arsenic, antimony and tin, lead, zinc, aluminium, and chromium, is divided into two portions, and treated as in (*b*) and (*c*).

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[1] *Zeitsch. anorg. Chem.*, **103**, 221.

(*b*) One portion of the filtrate from (*a*) is strongly acidified with hydrochloric acid, filtered if necessary, and treated in an Erlenmeyer flask with iron powder poor in carbon, and the escaping gas introduced into a hydrochloric acid solution of mercuric chloride (as *hydrogen arsenide* may be formed, caution is necessary here). A yellow precipitate indicates *arsenic*, and a white one *antimony*. The precipitate formed in the Erlenmeyer flask is filtered off, and the filtrate tested with mercuric chloride for *stannous ion*. The residue, which may contain antimony, lead, iron, and a little arsenic, is washed and then heated with concentrated nitric acid, *antimony pentoxide* being left.

(*c*) The second portion of the filtrate from (*a*) is heated with an excess of sodium sulphide. Lead and zinc ions are precipitated as sulphides, and chromic ion as hydroxide; the ions of arsenic, antimony, and tin dissolve as sulpho-anions, and aluminium ion as aluminate ion. The filtrate is dealt with as in (*f*).

(*d*) The separated precipitate from (*c*) is gently heated with hydrogen peroxide and treated with dilute sulphuric acid. Zinc and chromate ions dissolve, whilst lead remains undissolved as sulphate or sulphide. If it cannot be directly detected by its black colour, the separated precipitate is extracted with ammonium tartrate solution, and the solution thus obtained treated with sodium sulphide.

(*e*) *Zinc ion* is detected in the filtrate from (*d*) by precipitation with potassium ferrocyanide. *Chromate ion* may generally be recognised by the yellow colour of the filtrate obtained in (*d*), but otherwise may be detected in a separate portion of the filtrate by the blue coloration produced after acidification with sulphuric acid and treatment with hydrogen peroxide (ether being added).

(*f*) *Aluminium ion* is precipitated from the filtrate (*c*) by the introduction of carbon dioxide, and, if necessary, identified by dissolving it in hydrochloric acid, separating the silicon dioxide, and treating the liquid with ammonia.

(*g*) The precipitate obtained in (*a*) is dissolved by heating it with nitric acid and hydrogen peroxide (if necessary the solution filtered), and any residue examined in accordance with the course for insoluble substances, provided these have not been filtered off in (*a*)). The liquid is evaporated to dryness on the water bath (if phosphate ion is present, with the addition of tin), the residue taken up with water, and the precipitate [1] containing tin (antimony, arsenic), phosphate ion, and silicon dioxide filtered off.

The solution is treated with ammonia in excess and with hydrogen peroxide, heated for 10 minutes on the water bath in a covered vessel, and ammonium oxalate then added.

The precipitate, which contains iron, manganese, bismuth, barium, strontium, and calcium, is treated as in (*h*), the filtrate as in (*k*).

(*h*) The precipitate from (*g*) is boiled with sodium carbonate and sodium hypochlorite solutions, whereby *manganese* dissolves as permanganate ion.[2] The liquid is filtered, the residue treated with acetic acid,[3] and evaporated (without filtration) to dryness, the residue taken up with water, and the liquid filtered. The residue is treated as in (*i*); the solution contains barium, strontium, and calcium ions, which are separated by means of potassium chromate in the usual way.

(*i*) The residue from (*h*) is dissolved in sulphuric acid and hydrogen peroxide; one portion of the solution is tested for *ferric ion* by means of potassium thiocyanate, and another is reduced with stannous chloride and ferric ion and tested by means of potassium iodide for *bismuth ion*,[4] which may be recognised by the yellow coloration.[5]

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[1] Since it may contain iron and bismuth if too strongly heated, the precipitate is treated with strong hydrochloric acid (if their ions are not found in the solution), and tests for them applied to this solution.

[2] If, in the presence of chromate ion, the red colour cannot be recognised, the solution is heated, after the addition of ammonia; manganese separates as hydrated dioxide.

[3] The alkali earths dissolve herein, as their oxalates have been oxidised to carbonates by the hypochlorite.

[4] If desired, the quantity of manganous ion, which is only oxidised to permanganate ion to a small extent in (*h*), may be estimated by precipitating it as peroxide by heating the liquid with solid potassium persulphate before applying tests for ferric and bismuth ions.

[5] If a turbidity, due to silver, mercurous, or cuprous iodide is formed, it should be allowed to subside.

(*k*) The solution obtained in (*g*), which may still contain traces of barium ion, is treated with a few drops of sulphuric acid and filtered from any precipitated barium sulphate; the ammoniacal solution is treated with hydrazine sulphate, and allowed to stand for some hours in a moderately warm place. Silver and mercury are precipitated as metals, and are separated from one another as in (*l*). The filtrate is treated as in (*m*).

(*l*) The metallic residue is treated with *aqua regia*, the solution evaporated, and the residue taken up with water. *Silver* chloride is left, *mercuric* chloride dissolves and may be detected by means of stannous chloride.

(*m*) The filtrate obtained in (*k*) is boiled with sodium hydroxide and sodium hypochlorite solutions until all the ammonia has escaped; the precipitate is then dissolved in acetic acid, and sodium sulphite and potassium thiocyanate added; a precipitate indicates *copper ion*. The filtrate from this is divided into two portions.

(*n*) One portion is evaporated, treated with potassium thiocyanate, and shaken with amyl alcohol. The latter assumes an intense blue coloration in the presence of *cobalt ion*. The liquid is separated from the amyl alcohol in a separating funnel, and the aqueous solution tested for *magnesium ion* by means of ammonium phosphate.

(*o*) The second portion of the filtrate obtained in (*m*) is tested for *nickel ion* by boiling with dimethylgyloxime. The filtrate from it is rendered alkaline, and treated with potassium thiocarbonate, whereby *cadmium ion* separates in the form of a yellow precipitate.

B. Methods of separation for anions.

Really trustworthy methods of separation, based on the successive separation of the individual anions, have up to the present only been devised for certain groups, among them being the members of the second group of anions. Details of them will be found under the "*Summary and Remarks*" at the end of the respective sections. We confine ourselves here to the following remarks:—

H. Trey[1] has suggested groups which correspond in the main with the group divisions in this book: A. Anions precipitable by silver nitrate; (*a*) from nitric acid solution, (*b*) from neutral solution. B. Anions precipitable by barium chloride from mineral acid solution. C. Anions precipitable by barium and calcium chlorides from acetic acid solution. He recommends that tests to determine whether members of the individual groups are present should be applied in such a way that first, on the one hand, the acidified solution is treated with silver nitrate and the filtrate covered with a layer of ammonia solution, and, on the other hand, the acidified solution is treated with barium chloride, and calcium chloride added to the filtrate, which is then covered with a layer of sodium acetate solution. It is then possible to recognise at the points of contact of the layers, without the necessity of exact neutralisation, whether members of groups A, B, and C are present.

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[1] *Zeitsch. anal. Chem.*, **33**, **533.**

Separate tests must then be made for the detection of the individual members of the groups.

Frits Feigl[1] has suggested separating the anions into two groups by precipitation with zinc nitrate from alkaline solution, and then testing the precipitate and the solution separately by means of drop reactions.

The liquid is boiled with sodium carbonate (if alkali salts were not present from the start) and filtered, any ammonium ion present removed by boiling with sodium hydroxide, and nitric acid added (without neutralisation), with the subsequent addition of zinc nitrate in concentrated solution or solid form. The liquid is filtered, and there result:—

A. A precipitate of the zinc salts of S'', SO''_3, PO'''_4, BO'''_3, F', $Fe(CN)'''_6$, $Fe(CN)''''_6$, CN', (MoO''_4, VO'''_4, WO''_4).

B. A solution containing the zinc salts of CNS', Cl', Br', I', ClO'_3, SO''_4, $S_2O''_3$, (SO''_3).

Small quantities of the precipitate are transferred to a filter paper and treated successively with a drop of—

1. Acid lead nitrate solution: Yellowish-brown, but when passed through a flame black, indicates S''.
2. Sodium nitroprusside solution: A raspberry-red coloration indicates SO''_3
3. Acid ferrous salt solution: A bluish-green coloration indicates $Fe(CN)''''_6$.
4. Acid ferric salt solution: A dark blue coloration indicates $Fe(CN'''_6)$.
5. Stannous chloride solution: A yellow to brown coloration

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[1] *Zeitsch. anal. Chem.*, 57. 135.

indicates molybdate or tungstate ion. If neither sulphide nor sulphite are present, a test for cyanogen is made with—

6. Mercurous nitrate solution: A black coloration indicates CN′.
7. A portion is treated on turmeric paper with hydrochloric acid: If the paper is red when dried, becoming blackish-blue on treatment with potassium hydroxide, BO'''_3 is indicated.
8. A portion is examined by means of the etching test for F′.
9. A part of the precipitate is dissolved in nitric acid, and tested for PO'''_4 by means of ammonium molybdate.
10. If sulphide or sulphite is present, a little of the precipitate is heated with sulphuric acid in a porcelain crucible which is covered with a filter paper saturated with ammonium sulphide. Treatment with a drop of acid ferric salt solution produces a red coloration in the presence of cyanogen ion.

Small portions of the solution are tested:

(*a*) With ferric chloride: A red coloration indicates CNS′.

(*b*) With chlorine water and carbon bisulphide: A violet or brown coloration indicates I′ or Br′ respectively.

(*c*) With barium chloride: A precipitate of SO''_4, insoluble in hydrochloric acid, is formed.

If no sulphite ion was found in 2, tests are made—

(*d*) By the introduction of malachite green: Decolorisation indicates SO''_3.

(*e*) The remainder of the solution is treated at boiling point with lead nitrate, and filtered. The precipitate is treated with a drop of silver nitrate: A brownish-yellow coloration indicates $S_2O''_3$.

(*f*) The filtrate is acidified with nitric acid, and silver nitrate then added; the precipitate of Cl′(Br′, I′) is digested with sodium arsenite solution, the liquid filtered, and the filtrate tested for Cl′ by acidification with nitric acid.

(*g*) The filtrate from the silver precipitation in (*f*) is reduced with sulphur dioxide, and the Cl′ produced from ClO'_3 detected in the nitric acid solution by means of silver nitrate.

APPENDIX

I

Behaviour of the most important Alkaloids towards Reagents, and Systematic Course for their Identification.

THE detection of alkaloids by means of reagents, and still more their separation, is incomparably more difficult than the differentiation and identification of most inorganic cations In the case of many alkaloids the compounds, in the form of which they can be separated from others, are somewhat too soluble for the purpose of effecting sharp separations, whilst in the case of others we are only acquainted with the external phenomena of the reactions, and this is particularly applicable to the colour reactions, but cannot yet attribute them to their causes, so that we therefore lack exact knowledge of all the conditions which have a modifying influence on the occurrence of a reaction. If these remarks apply even to the pure alkaloids, they are still more applicable to the not completely pure alkaloids, such as are often obtained when they are isolated from food, cadaveric remains, etc.

Under certain conditions these difficulties are intensified in two ways. In the first place, there are alkaloids which cannot be identified with certainty by means of *chemical* reactions, so that *physiological tests* must be used for their identification. Thus, for example, atropine can only be definitely identified by its mydriatic action (enlarging effect upon the pupil) when its solution is introduced into the conjunctival sac of the eye of a man or a cat or of the isolated eye of a frog. In the second place, there are formed in putrefying cadaveric remains, and sometimes also in normal or pathological urine, substances which behave like alkaloids, and frequently resemble some of them in their reactions in such a way that there is a possibility of their being mistaken for them. These substances, which have been investigated especially by Selmi, Nencki, Brieger, and Kratter, are termed *ptomaines* or *cadaveric alkaloids*, and frequently also *putrefaction bases*. The researches of Brieger and

Kratter, however, have shown that the ptomaines only give misleading reactions when they are used in incompletely purified condition, *i.e.* in the form of the syrupy residue containing peptones, which is left on evaporating the extracts obtained in the course of the examination of bodies (Sec. 229, *c*). In the pure condition, however, most of them do not give any characteristic colour reactions. *It is, therefore, of the utmost importance that suspicious substances obtained in the course of an examination should be thoroughly purified before being subjected to chemical or physiological tests.*

As an introduction to this branch of qualitative analysis, we have added Appendix I., for which, however, we do not claim completeness, preferring to restrict ourselves to the alkaloids of most importance and those most frequently used. Among these we include the following: Nicotine, coniine, morphine, cocaine, narcotine, quinine, cinchonine, strychnine, brucine, veratrine, and atropine.

When the methods of identifying and separating these have been learned, it will not be a difficult matter to extend the scheme to other alkaloids in a given case.

The appendix on the alkaloids is divided into the following headings:—

A. General reagents for alkaloids.

B. Properties and reactions of individual alkaloids, arranged in groups in accordance with their analytical characteristics.

C. Properties and reactions of certain non-nitrogenous substances, which closely resemble alkaloids in their toxicological behaviour, or may be used for the adulteration of alkaloids, notably salicine, digitaline, and picrotoxine.

D. Systematic course for the detection of the alkaloids, etc., here taken into consideration:

(*a*) When only one may be assumed to be present.

(*b*) When several or all of them may be assumed to be present.

(*c*) When other organic substances are present.

A. General Reagents for Alkaloids.

Sec. 209.

Under the name of "general reagents" are to be understood such as precipitate all, or nearly all, of the alkaloids. They are, therefore, particularly suitable for determining whether an alkaloid is present in a solution, and may be used for the separation of alkaloids from their solutions, but do not afford the means of *differentiating* between the different alkaloids, or only to a limited extent. The reactions, however, only give certain results with *pure* solutions of alkaloids; in particular, the presence of colloids, such as gum arabic, interferes with the occurrence of several of the reactions. Such interfering foreign organic substances must, therefore, be removed, if necessary by dialysis, before applying the reaction (J. Lefort and P. Thibault).

Of the general reagents the most important are:—

A solution of iodine in potassium iodide solution (Wagner[1]); platinum chloride; gold chloride; mercuric chloride; potassium mercuric iodide (v. Planta,[2] Mayer[3]); potassium cadmium iodide (Marmè[4]); potassium bismuth iodide (Dragendorff[5]); phosphomolybdic acid (de Vrij, Sonnenschein[6]); phosphoantimonic acid (Fr. Schulze[7]); phosphotungstic acid (Scheibler[8]); picric acid (H. Hager[9]); tannic acid (tannin).

The *most important* of these reagents are potassium bismuth iodide, phosphomolybdic acid, and tannic acid (Gadamer).

In making a test, a drop of the solution containing the alkaloid is placed on a clock-glass, a drop of a solution of the reagent placed beside it by means of a glass rod, and the two drops mixed by gently shaking the clock-glass with a rotatory movement.

Iodine in potassium iodide solution (Wagner's reagent): Originally a solution of five parts of iodine and ten parts of potassium iodide in 100 parts of water was used; more recently C. Kippenberger[10] has recommended the use of N/10 iodine solution (containing 12·7 grms. of iodine and 60 grms. of potassium iodide per litre). The reagent produces in neutral or slightly acid solutions of alkaloids flocculent brown precipitates of alkaloid periodide hydriodides of the general formula $\text{Alk.I}_2\text{.HI}$. Their formation and separation is promoted by acidifying the solutions with sulphuric acid. If the precipitate is dissolved, after washing, in an aqueous solution of sulphur dioxide, and the solution evaporated on the water bath to remove the excess of sulphur dioxide and hydriodic acid, the base is left in combination with sulphuric acid. If the precipitate was produced in a solution which contained a large proportion of organic acids, it should be dissolved in a dilute solution of sodium thiosulphate, the liquid filtered, iodine solution again added to the filtrate, and the fresh precipitate thus obtained treated as described above. If the brownish-red precipitate produced by iodine-potassium iodide solution in a solution of a strychnine salt is dissolved in alcohol containing sulphuric acid, and the solution allowed to evaporate, crystalline rods of strychnine periodate sulphate (with pronounced polarising action) are obtained (de Vrij and van der Burg[1]). With regard to quinine periodide sulphate, *cf.* Sec. 217, 11.

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[1] *Zeitsch. anal. Chem.*, **4**, 387.

[2] "*Das Verhalten der wichtigsten Alkaloide gegen Reagenzien*," Heidelberg, 1846.

[3] *Vierteljahrsch. f. Pharm.*, **13**, 43.

[4] *Zeitsch. anal. Chem.*, **6**, 123.

[5] *Ibid.*, **5**, 406.

[6] *Ann. d. Chem. u. Pharm.*, **104**, 45.

[7] *Ibid.*, **109**, 179.

[8] *Zeitsch. anal. Chem.*, **12**, 315.

[9] *Pharm. Zentralh.*, **10**, 131.

[10] *Zeitsch. anal. Chem.*, **35**, 412 (1895).

Platinum chloride is used in the form of a neutral solution of one part in twenty parts of water. It forms compounds with alkaloid hydrochlorides analogous to ammonium platinochloride. Some of these are only sparingly soluble in water, others dissolve fairly readily. The platinochlorides are most certainly and most quantitatively obtained when the solutions are evaporated nearly to dryness with sufficient platinum chloride, and the residue treated with alcohol. The compounds are yellowish-white or yellow; some are crystalline and others flocculent; and most of them dissolve more readily in hydrochloric acid than in water.

Auric chloride in neutral aqueous solution (1 : 30) gives with alkaloid hydrochlorides, in not too dilute solution, yellow or brown amorphous or crystalline precipitates of aurochlorides. Some of these easily decompose, with the separation of metallic gold.

Mercuric chloride. C. Kippenberger considers a solution of 13·55 grms. per litre the most suitable; other authorities use a solution of 50 grms. per litre. The reagent gives with many alkaloid salts white or yellowish precipitates, which are usually amorphous, but gradually become crystalline. The compounds of brucine, strychnine, codeine, and thebaine are practically insoluble, whilst those of veratrine, narcotine, atropine, and narceine dissolve fairly readily. The presence of mineral acids does not prevent the reaction, but acetic acid and alcohol are injurious. A large excess of mercuric chloride must be avoided, since many of the compounds may then be dissolved (C. Kippenberger[2]).

Potassium mercuric iodide solution (Mayer's reagent). This is prepared by dissolving 13·55 grms. of mercuric chloride in a concentrated solution of 50 grms. of potassium iodide, and diluting the liquid to a litre. The reagent gives a precipitate with solutions of the salts of all the alkaloids. The precipitates are white to yellowish-white and insoluble in water and dilute hydrochloric acid.

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[1] *Liebig u. Kopps Jahresber.*, 1857, 602.

[2] *Grundlagen fur den Nachweis von Giftstoffen*, 1897, 100.

Potassium cadmium iodide solution. This is prepared by dissolving 10 grms. of cadmium iodide in a boiling solution of 20 grms. of potassium iodide in 60 c.c. of water. After the solution is complete, the liquid is diluted with an equal volume of a cold saturated solution of potassium iodide. The reagent produces precipitates in very dilute solutions of alkaloid salts acidified with sulphuric acid. The precipitates are white or yellowish-white and flocculent, although some of them soon become crystalline. They are insoluble in ether, readily soluble in alcohol, but less soluble in water, and dissolve readily in excess of the precipitant. The precipitates have a tendency to decompose after standing for some time. The alkaloids may be separated from the undecomposed precipitates by treatment with aqueous solutions of alkali carbonates or hydroxides, and shaking the liquids with solvents suitable for the extraction of alkaloids, but not miscible with water (benzene, amyl alcohol, ether, etc.).

Potassium bismuth iodide solution (Dragendorff's reagent). Bismuth iodide is introduced into a hot concentrated solution of potassium iodide so long as it dissolves, the liquid filtered while hot, and the filtrate diluted with an equal volume of a cold saturated solution of potassium iodide. The resulting orange-coloured liquid is stable ; when kept it should be protected from the light. According to Thoms [1] the reagent may also be prepared by dissolving 80 grms. of bismuth subnitrate in 200 c.c. of nitric acid of sp. gr. 1·18, and pouring this liquid slowly and with stirring into a *concentrated* solution of 272 grms. of potassium iodide in water, whereby the brown precipitate first formed dissolves to form a yellowish-red solution. The liquid is allowed to stand for several days in as cold a place as possible (an ice chest), and is then decanted from the crystallised potassium nitrate, and diluted to one litre. When added, drop by drop, to aqueous solutions of alkaloid salts, acidified with sulphuric acid (10 c.c. of the alkaloid salt solution with 5 drops of concentrated sulphuric acid) the reagent produces almost immediately flocculent orange precipitates with nicotine, coniine, morphine, cocaine, narcotine, quinine, and cinchonine, strychnine, brucine, atropine, and most other alkaloids. Veratrine solutions, however, show only a slight turbidity. The precipitates obtained with the first-mentioned alkaloids become somewhat agglomerated on heating ; on continuing the heating for some time they dissolve, but the greater portion of the compounds separates again on cooling. None of the precipitates is crystalline. The separation of the alkaloids from the precipitates may be effected as in the case of those produced by potassium cadmium iodide.

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[1] *Zeitsch. anal. Chem.*, **47**, 269 (1908).

Phosphomolybdic acid solution (Sonnenschein's reagent). Disodium hydrogen phosphate solution is treated with the ordinary ammonium molybdate reagent (p. 111), and the precipitate well washed, first with 5 per cent. ammonium nitrate solution, and afterwards with cold water. It is then mixed with a little water, and dissolved by the addition of the smallest possible quantity of hot sodium carbonate solution. The resulting solution is evaporated, and the residue ignited until all ammonia has been expelled, and then dissolved in ten times its quantity of water. This solution is treated with nitric acid in sufficient quantity to dissolve the precipitate first formed. The reagent precipitates all the alkaloids (but also ammonia and amines) from their acid solutions, and in most cases even from very dilute solutions. The precipitates are amorphous, pale yellow, ochre-yellow, or brownish-yellow, and are insoluble or only very sparingly soluble in water, alcohol ether, and dilute acids, with the exception of phosphoric acid, at the ordinary temperature, being most insoluble in dilute nitric acid, especially when a little of the reagent is also present; acetic acid is also practically without influence, but has a solvent action when hot. The precipitates are readily soluble in solutions of alkali hydroxides or alkali carbonates, usually with the separation of the alkaloid; they are also decomposed, with liberation of the alkaloid, when acted upon for some time by alkaline earths, silver oxide, lead oxide, and carbonates of those metals. The liberated alkaloids may then be extracted by treatment with suitable solvents (ether, amyl alcohol, benzene, etc.).

Phospho-antimonic acid solution (Schulze's reagent). Antimony pentachloride is added drop by drop to a concentrated aqueous solution of phosphoric acid. The reagent prepared by Schulze's original method of introducing 10 grms. of antimony pentachloride into 40 grms. of a saturated solution of sodium hydrogen phosphate is less stable; a large deposit of pyroantimonic acid is soon formed (R. Otto). The solution, like the phosphomolybdic acid solution, precipitates ammonia and most alkaloids, but does not precipitate caffeine. The reactions are sensitive, but in the case of most alkaloids, and notably nicotine and caffeine, are less sensitive than the phosphomolybdic acid reactions; only in the case of atropine is phospho-antimonic acid the more sensitive reagent. As a rule, the precipitates are flocculent and whitish, but the brucine precipitate is pink. When heated the latter dissolves, but separates again, on cooling, from the liquid, which remains of an intense crimson colour.

Phosphotungstic acid solution (Scheibler's reagent). Six parts of commercial sodium tungstate ($Na_2Wo_4.2H_2O$) are dissolved in 16 parts of water, and the solution treated with 5 parts of a 20 per cent. solution of phosphoric acid (1·12). The reagent precipitates all alkaloids from their solutions, the precipitates being flocculent and white. The reactions are very sensitive. Acid solutions containing only $\frac{1}{200000}$ of strychnine or $\frac{1}{100000}$ of quinine still show a distinct turbidity: if flocculent deposits subside, after standing for 24 hours, they may be separated and washed with slightly acidified water without passing through the filter. The precipitates are decomposed by calcium hydroxide or barium hydroxide, with the formation of insoluble phosphotungstic acid salts, and separation of the alkaloids

Picric acid is used in 1 per cent. aqueous solution. It precipitates nearly all the alkaloids as picrates, even from solutions strongly acidified with sulphuric acid. The precipitates, which are crystalline or soon become so, are yellow, and, in most cases, are insoluble in excess of picric acid solution; in the case of the majority of alkaloids they are formed even in very dilute solutions. The exceptions are given in the description of the individual alkaloids.

Tannic acid (*tannin*) *solution*. A freshly prepared solution of one part of tannin (free from gallic acid) in eight parts of water and one part of alcohol produces flocculent, white, or yellowish precipitates in neutral or very slightly acid solutions of alkaloids. Morphine is not precipitated, or only to an insignificant extent.

B. Properties and Reactions of Individual Alkaloids.

(a) Volatile alkaloids.

The volatile alkaloids are liquid at the ordinary temperature, and may be volatilised either in the pure condition or with water. Hence, they are obtained in the distillate when their salts are distilled with strong non-volatile bases and water. Their vapours form fumes when brought into contact with those of volatile acids.

SEC. 210.

1. Nicotine, $C_{10}H_{14}N_2$.

β-Pyridyl-n-methyl-α-pyrrolidine, $C_5H_4N.C_4H_7N(CH_3)$.

1. *Nicotine*, which occurs in association with other alkaloids in the leaves and seeds of the tobacco plant (*Nicotiana tabacum* and

rustica), is, when absolutely pure, a colourless oily liquid, which becomes slightly yellow or brown through the action of the air. Its specific gravity compared with water at 4° is 1·01837 at 10·2°, and 1·01101 at 20° (Landolt).[1] It boils in an atmosphere of hydrogen at 246·2° (Fl. Ratz)[2] under a pressure of 719·8 mm., without undergoing decomposition. When heated to boiling point in the air, it is partially decomposed. Natural nicotine rotates a beam of polarised light to the left. Ratz found a particularly pure preparation to have $[\alpha]_D = -169°$.

It is miscible with water in all proportions. Potassium and sodium hydroxides precipitate it from its solution. It is readily soluble in alcohol, ether, amyl alcohol, and petroleum spirit.

Nicotine has a penetrating odour of tobacco, which is particularly pronounced on heating. It has a sharp burning taste and is very poisonous. Applied to paper, it produces a transparent stain which slowly disappears; it turns turmeric paper brown and red litmus paper blue. These reactions are more distinct with concentrated aqueous solutions of nicotine than with the pure alkaloid.

2. Nicotine has the character of a fairly strong mono-acid base; it precipitates hydroxides from solutions of metallic salts, and combines with acids to form *salts*. The latter are non-volatile, or only slightly volatile; they are readily soluble in water and alcohol (with the exception of nicotine acetate), but are insoluble in ether, amyl alcohol, chloroform, benzene, and petroleum spirit; some of them can be crystallised. They are odourless, but have a strong taste of tobacco. Their solutions can be evaporated at a moderate heat, without any considerable loss of nicotine. Nicotine hydrochloride (unlike coniine hydrochloride) only crystallises with difficulty. It forms a deliquescent crystalline mass, which, on evaporating its solution, volatilises, with partial decomposition, into its components (A. Pinner). The salts, when distilled with potassium hydroxide solution, yield a distillate containing nicotine. If this distillate is neutralised with oxalic acid and evaporated, there is left a residue of nicotine oxalate, which may be separated from any ammonium oxalate present by means of alcohol, in which the former salt is soluble and the latter insoluble.

3. On shaking an aqueous solution of nicotine, or a solution of a nicotine salt to which potassium or sodium hydroxide has been added, with *ether* or *petroleum spirit*, the nicotine will be extracted.

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[1] *Ann. d. Chem.*, **189**, 319.

[2] *Wiener Monatsh.*, **26**, 1241 (1905).

Owing to the ready solubility of nicotine in water, however, its transference to the extraction-solvent is far from being quantitative. The greater the amount of alkali hydrochloride added to the solution, the more complete is the extraction. It is advisable to repeat the shaking several times with fresh portions of ether or petroleum spirit. If the resulting solution is allowed to evaporate on a clock-glass at about 20°–30° the nicotine is left in drops and streaks. On heating the glass, the drops volatilise as a white vapour with a strong odour. If an ethereal solution of hydrogen chloride is added to the liquid to be evaporated, nicotine hydrochloride is left as an amorphous yellow residue, which only becomes crystalline after standing for a long time.

4. *Concentrated sulphuric acid and nitric acid* of sp. gr. 1·2 dissolve nicotine in the cold, yielding colourless solutions, whilst cold *nitric acid* of sp. gr. 1·4 dissolves it to form a red solution.

5. On gently heating a drop of nicotine with three or four drops of hydrochloric acid of sp. gr. 1·12 a pale brownish-red solution is obtained. When this is treated, after cooling, with a drop of *nitric acid* of sp. gr. 1·4 it becomes violet-red and then gradually red.

6. A solution of *iodine* in *potassium iodide solution*, when added in *small* proportion to an aqueous solution of nicotine, produces a yellow precipitate, which disappears after some time. On adding more iodine solution an abundant red precipitate is produced; a similar precipitate is also formed in solutions of nicotine salts. These precipitates also disappear after some time.

7. *Platinum chloride* produces a whitish-yellow precipitate in aqueous solutions of nicotine or nicotine salts, which are not too dilute. The precipitate is flocculent at first. When the liquid containing it is heated the precipitate dissolves, but, on continuing the heating, is soon re-precipitated as a heavy crystalline orange-yellow powder, which is seen under the microscope to be composed of round crystalline granules. If a fairly dilute aqueous solution of nicotine is treated with excess of hydrochloric acid and then with platinum chloride the liquid remains clear at first. After some time, however, the platinochloride separates in minute crystals (pointed quadrilateral rods) visible even to the naked eye. An alcoholic solution of nicotine containing free hydrochloric acid is immediately coloured yellow by platinum chloride. The salt thus obtained is a finely-granular powder.

8. *Auric chloride*, when added in excess, produces in solutions of nicotine salts, as also in an aqueous solution of nicotine, a flocculent

reddish-yellow precipitate, which dissolves with difficulty in hydrochloric acid. In the presence of excess of nicotine the precipitate is not formed.

9. On adding an aqueous solution of nicotine to an excess of *mercuric chloride solution* there is produced an abundant flocculent white precipitate, which is soluble in hydrochloric acid and in ammonium chloride solution. A neutral solution of nicotine hydrochloride, but not one containing an excess of acid, also gives a precipitate with mercuric chloride.

10. On treating an aqueous or alcoholic solution of nicotine with *silver nitrate solution* the liquid assumes a faint brown coloration, which gradually becomes brown, and finally, after a long time, a brownish-black precipitate is formed.

11. *Picric acid*, when added in excess to an aqueous solution of a neutral nicotine salt, gives a yellow precipitate. This precipitate is crystalline or soon becomes so, and is soluble in hydrochloric acid.

12. A solution of *tannic acid* gives an abundant white precipitate with aqueous solutions of nicotine. On adding hydrochloric or dilute sulphuric acid to the liquid the precipitate is dissolved.

13. When an ethereal solution of nicotine is mixed with an equal volume of an **ethereal solution of iodine**, and the mixture allowed to stand in a closed dry test-tube, there separates a brownish-red resinous oil, which gradually solidifies to a crystalline mass. On allowing the light brownish-yellow supernatant liquid to stand, long transparent ruby-red crystals (shimmering blue in reflected light) shoot through it (*Roussin's crystals*). According to C. Kippenberger,[1] these consist of the hydriodic acid salts of nicotine monoiodide, $C_{10}H_{13}IN_2$, and of periodides of this salt. Under certain conditions of concentration Kippenberger sometimes obtained pale yellow crystals, in addition to Roussin's crystals. The reaction is very characteristic, but unfortunately requires a considerable amount of material. In the case of a solution of 0·08 grm. of nicotine in 40 grms. of ether (1 : 500) the crystals only appear after about 4 hours; whilst in a solution of 1 : 150 or 1 : 100 they appear after a few minutes (Dragendorff and Zalewsky). As a rule, old resinified nicotine no longer gives the crystals (W. Autenrieth).

14. On adding an alcoholic solution of nicotine to 2 to 3 c.c. of **epichlorhydrin,** and heating the mixture until it boils, the solution becomes deep red (distinction from coniine). The lower limit of sensitiveness for the reaction is reached with the use of 5 drops of a

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[1] *Zeitsch. anal. Chem.*, **42**, 232 (1903).

solution of 1 : 500. The reaction is then obtained only after long continued boiling (H. Melzer[1]).

15. If unresinified nicotine is heated with one drop (more causes explosion) of a 30 per cent. solution of **formaldehyde** (free from formic acid), and the resulting solid residue treated, after a few hours, with a drop of concentrated nitric acid, an intense pink to red coloration is produced. A distinct reaction is given by as little as 0·5 mgrm. of nicotine. The test succeeds as well, or even better, when pure *formic acid* is used instead of formaldehyde. Coniine does not give the reaction (Schindelmeiser[2]).

16. According to Dragendorff and Zalewski, the *general reagents* for alkaloids show the following limits of sensitiveness when applied to 0·1 c.c. of a neutral solution of a nicotine salt: Platinum chloride, 1 : 5000; auric chloride, 1 : 10,000; phosphomolybdic acid, 1 : 40,000; potassium bismuth iodide, 1 : 40,000; potassium mercuric iodide, 1 : 15,000; mercuric chloride, 1 : 1000; tannic acid, 1 : 500; and iodine in potassium iodide solution, 1 : 3000.

SEC. 211.

2. Coniine, $C_8H_{17}N$.

a-Propylpiperidine, $C_5H_{10}(C_3H_7)N$.

1. *Coniine* occurs, together with small quantities of other allied alkaloids, in the seeds, especially when unripe, and also in other parts of the spotted hemlock (*Conium maculatum*). It is a colourless oily liquid with a repulsive stupefying odour and a pungent taste. According to Zalewsky the mouse-like odour of dilute solutions of coniine does not belong to it, but is due to impurities, possibly decomposition products of the alkaloid. On exposure to the air coniine becomes brown and viscid. It has a specific gravity of 0·845 at 20°, and boils at 168·5°. Even at the ordinary temperature it volatilises to a considerable extent. It distils without alteration in a current of hydrogen, but when distilled in vessels containing air it turns brown, and is partially decomposed; it is readily volatile in a current of steam. It dissolves with difficulty in water, 90 parts at the ordinary temperature dissolving one part of coniine. It is much less soluble in hot water, so that a cold saturated solution becomes milky when heated and clear again on cooling. Coniine

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[1] *Zeitsch. anal. Chem.*, **37**, 357 (1898).

[2] *Pharm. Zentralh.*, **40**, 703 (1899).

is miscible with alcohol in all proportions; it also dissolves readily in ether, petroleum spirit, and essential and fatty oils, but is less soluble in chloroform (H. Melzer[1]). Solutions of natural coniine rotate a beam of polarised light to the right $[\alpha]_D = +13{\cdot}8°$. Aqueous and alcoholic solutions show a pronounced alkaline reaction.

2. Coniine is a strong mono-acid base; like ammonia, it precipitates hydroxides from solutions of metallic salts, and combines with acids to form *salts*. The latter are soluble in water and alcohol, insoluble in petroleum spirit, and insoluble, or practically so, in ether. Coniine produces dense white fumes with volatile acids. **Coniine hydrochloride crystallises readily**; if a trace of coniine is dissolved in one or two drops of concentrated hydrochloric acid, and the solution evaporated, colourless or slightly yellow crystals are immediately obtained, the characteristic form of which, in pointed needles or rods grouped into stars or angular aggregates, may be recognised under a magnification of 180 to 250 diameters. (Distinction from nicotine.) Coniine hydrochloride is readily soluble in absolute alcohol. (Distinction and method of separation from ammonium chloride, W. Lenz.) Solutions of coniine sulphate yield first needle-shaped and subsequently large leaf-like crystals (Dragendorff). The salts, when dry, have no odour of coniine, and only a faint one when moist, but on adding sodium hydroxide a pronounced odour is developed; on then distilling the liquid the distillate will contain coniine. If this distillate is neutralised with oxalic acid and evaporated, and the residue treated with alcohol, the coniine oxalate will dissolve, whilst any ammonium oxalate present will remain undissolved.

Since coniine is only slightly soluble in water, and still less soluble in aqueous solutions of alkalis, a concentrated solution of a coniine salt becomes milky on the addition of sodium hydroxide. The drops which first separate gradually unite and collect upon the surface.

3. When an aqueous solution of a coniine salt is shaken with *sodium hydroxide* and *ether* or *petroleum spirit*, the coniine will be extracted by these solvents. On then allowing the extract to evaporate on a clock-glass at about 20° to 30°, the coniine will be left in the form of oily yellow drops.

4. Coniine dissolves in cold concentrated *sulphuric acid* and in cold *nitric acid* of sp. gr. 1·4 without producing a coloration.

5. Coniine behaves like nicotine towards solutions of *iodine with potassium iodide* and of *tannic acid.*

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[1] *Arch. d. Pharm.*, **236**, 701.

6. *Platinum chloride* produces a precipitate only in concentrated solutions of coniine hydrochloride; in dilute solutions no precipitate is formed, even on the addition of alcohol. (Essential distinction from nicotine.)

7. *Auric chloride* produces a yellowish-white precipitate, but only in concentrated solutions of coniine hydrochloride; the precipitate is insoluble in hydrochloric acid.

8. *Mercuric chloride* precipitates coniine as a white precipitate soluble in hydrochloric acid.

9. *Silver nitrate* produces immediately a grey-brown precipitate in either aqueous or alcoholic solutions of coniine.

10. On treating coniine with water, and adding *chlorine water*, an abundant white precipitate, readily soluble in hydrochloric acid, is produced (Distinction from nicotine.) R. Otto could not always obtain this reaction.

11. When coniine is treated with water, and saturated solution of *picric acid* added, a yellow precipitate is formed; no precipitation takes place, however, in a dilute solution.

12. On treating a few c.c. of an alcoholic solution of coniine with five drops of *carbon bisulphide*, and allowing the mixture to stand for some minutes, it shows a more or less pronounced yellow coloration. On then adding two or three drops of a dilute aqueous solution of *copper sulphate* (1 : 200), a yellow to brown precipitate or coloration is produced, according to the concentration. The reaction is obtained even with 2 c.c. of a solution of 1 : 10,000 (H. Melzer[1]).

13. When a few drops of a solution of 1 grm of potassium permanganate in 200 grms. of concentrated sulphuric acid are mixed with a little coniine, the green coloration first produced changes to a violet coloration, which remains unchanged on further addition of sulphuric acid (D. Vitali and C. Stroppa[2]).

14. Using 0 1 c.c. of a neutral solution of coniine sulphate, Dragendorff and Zalewsky found the *general reagents* for alkaloids to have the following degrees of sensitiveness: Phosphomolybdic acid, 1 : 5000; potassium bismuth iodide, 1 : 6000; potassium mercuric iodide, 1 : 1000; tannic acid, 1 : 100; platinum chloride, auric chloride, and mercuric chloride, less than 1 : 100; and iodine in potassium iodide solution, more than 1 : 10,000.

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[1] *Zeitsch. anal. Chem.*, **37**, 354 (1898)

[2] *Zeitsch. Unters. Nahr. Genuss.*, **3**, 687 (1900).

SEC. 212.

Summary and Remarks on the Volatile Alkaloids.

The volatile alkaloids are most easily identified in the pure condition. Hence, steps must first be taken to obtain them in such condition. The method of doing this, in the case of nicotine and coniine, has already been outlined above. The aqueous solution containing them is treated with sodium hydroxide and distilled in a current of hydrogen, and the distillate is neutralised with oxalic acid and evaporated. The residue is taken up with water, the solution treated with sodium hydroxide, and shaken with ether or petroleum spirit, and the extract containing the alkaloids allowed to evaporate at 20°. Coniine is distinguished from nicotine, in particular, by its odour, by its very slight solubility in water, the behaviour of the aqueous solution when heated, the rapid crystallisation, crystalline form and optical behaviour of its hydrochloride, and its behaviour towards silver nitrate, platinum chloride, chlorine water, and picric acid, and towards carbon bisulphide and copper sulphate. Nicotine is characterised by its behaviour when heated with hydrochloric acid, followed by treatment with nitric acid, but especially by its behaviour towards an ethereal solution of iodine, and towards epichlorhydrin. Lastly, it should be borne in mind that the general reagents for alkaloids precipitate nicotine from much more dilute solutions than coniine. In forensic cases, in the case of coniine in particular, a physiological test of identification (paralysis of the peripheral nerves) should be made by a qualified expert.[1]

(*b*) *Non-volatile alkaloids.*

The non-volatile alkaloids are solid, and cannot be distilled in a current of steam.

First Group.

Non-volatile Alkaloids, which are precipitated from their solution by Potassium or Sodium Hydroxide, and not redissolved on addition of excess of the precipitant.

Of the alkaloids described here morphine and cocaine belong to this group.

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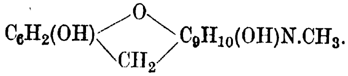
[1] Further chemical methods of differentiating between nicotine and coniine have been given by C. Reichard (*Pharm. Zentralh.*, **46**, 252 and 309 (1905)).

Sec. 213.

1. Morphine, $C_{17}H_{19}NO_3$.



$$C_6H_2(OH)\left\langle\begin{matrix} O \\ CH_2 \end{matrix}\right\rangle C_9H_{10}(OH)N.CH_3.$$

1. *Morphine* occurs, together with the alkaloids codeine, thebaine, papaverine, narcotine, narceine, and about ten others, and also with meconic acid and the inert nitrogenous compounds meconine and meconoisine, in *opium*, the dried latex of the green seed capsules of the poppy (*Papaver somniferum*). Crystalline morphine, $C_{17}H_{19}NO_3.H_2O$, is usually in the form of lustrous transparent needles, short rhombic rods, or (when obtained by precipitation) a white crystalline powder with a bitter taste. According to the determinations of M. Scholtz[1] and R. Maych,[2] the solubility of morphine is as follows: 1 part in 5000 parts of water at 15°, and in 500 parts at 100°; in 7630 parts of ether at 20°; in 10,600 parts of ether saturated with water; in 1600 parts of benzene; in 1525 parts of chloroform; in 1170 parts of petroleum spirit; in 781 parts of acetone; in 537 parts of acetic acid; in 300 parts of alcohol; in 100 parts of amyl alcohol at 17·5 (and still more readily in the boiling solvent); and in 4·8 parts of a saturated aqueous solution of chloral hydrate. The solutions in hot alcohol, as also those in hot water, have a distinctly alkaline reaction and a bitter taste. Morphine is extracted from them by freshly ignited bone charcoal (M. J. Lefort), and also by fuller's earth prepared in a specified manner (J. V. Lloyd[3]). Morphine has a lævo-rotation: $[\alpha]_D = -98{\cdot}4°$. Crystallised morphine loses its water of crystallisation at as low as 90° to 100°, and when carefully heated at a higher temperature (not much below 230°) it may melt and sublime without decomposition (Hesse). In alkaline solution morphine is converted by the action of atmospheric oxygen into oxydimorphine (pseudo-morphine), $C_{34}H_{36}N_2O_6.3H_2O$.

2. Morphine neutralises acids completely, combining with them to form *morphine salts*. Most of these are crystalline; they are readily soluble in water, and most of them also in alcohol (the sulphate requires 700 parts of cold and 144 parts of boiling alcohol of sp. gr. 0·82), but are insoluble in ether, chloroform, and amyl alcohol; they have a nauseous bitter taste. Freshly ignited bone charcoal

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[1] *Arch. d. Pharm.*, **250**, 418 (1912).

[2] *Zeitsch. anal. Chem.*, **39**, 119 (1900).

[3] *Cf.* W. Ostwald, *Die Welt in vernachlässigten Dimensionen*, 2nd ed., 1916, pp. 99 and 194.

extracts morphine from solutions of its salts (Dragendorff). Morphine and morphine salts are poisonous.

3. *Potassium hydroxide*, *sodium hydroxide*, and *ammonia* precipitate morphine from solutions of morphine salts (in most cases only after some time) in the form of a white crystalline powder. The separation is promoted by stirring, and by rubbing the sides of the vessel below the liquid. The precipitate dissolves very readily in exces of potassium or sodium hydroxide solutions, but with more difficulty in ammonia solution; it is also soluble in ammonium chloride and ammonium carbonate solutions, but only with difficulty in the latter. On shaking a solution of morphine in potassium or sodium hydroxide solution with petroleum spirit no morphine is extracted, and only a small proportion by shaking it with ether, but practically the whole of the alkaloid is extracted by shaking the liquid with warm amyl alcohol.

4. *Potassium carbonate and sodium carbonate* produce a precipitate of the same composition as do potassium or sodium hydroxides or ammonia. It is insoluble in excess of the precipitant. Hence, on adding potassium or sodium hydrogen carbonate to a solution of morphine in potassium or sodium hydroxide solution, or introducing carbon dioxide into the solution, morphine separates, especially after boiling the liquid, as a crystalline powder, containing water of crystallisation. When viewed with a lens this is seen to consist of small pointed crystals; under a magnification of 100 diameters these appear as rhombic rods.

5. **Sodium hydrogen carbonate** and **potassium hydrogen carbonate** precipitate hydrated morphine as a crystalline powder in a very short time from solutions of neutral morphine salts. The precipitate is insoluble in excess of the precipitant. A precipitate is not formed in the cold in acidified solutions.

6. When morphine or a morphine compound in solid form or in concentrated solution is brought into contact with strong *nitric acid* a yellowish-red liquid is obtained. A violet coloration is not formed on the addition of stannous chloride. (Distinction from brucine.) Dilute solutions do not change their colour on the addition of nitric acid in the cold, but when heated become yellow.

7. Absolutely pure *concentrated sulphuric acid* dissolves morphine in the cold, forming a colourless solution.[1] If a trace of *potassium*

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[1] W. Göhlich (*Zeitsch. anal. Chem.*, **40**, 749) found that out of 52 samples of commercial morphine hydrochloride not a single one answered the requirement of remaining unchanged by concentrated sulphuric acid.

nitrate is added to the freshly prepared solution, a coloration is produced, which is sometimes momentarily reddish, soon changing to brown, but is often immediately brown. If, on the other hand, a solution of morphine in concentrated sulphuric acid is allowed to stand for 12 to 15 hours in the cold, or is heated for half an hour at 100°, it undergoes a material alteration. This may be recognised by a pale dirty violet coloration, but especially by the fact that when the cold or cooled solution is now brought into contact on a porcelain surface with a trace of *potassium nitrate*, or with a drop of *nitric acid* of sp. gr. 1·2, it assumes a fine coloration which is sometimes violet and then blood-red, but may also be blood-red immediately. It fades slowly to orange-yellow. In the presence of extremely minute traces only a pink coloration is produced (A. Husemann[1]). The reaction is very characteristic and also very sensitive; it was found by Kauzmann and Dragendorff[2] to be capable of detecting as little as 0·01 to 0·02 mgrm. of anhydrous morphine sulphate.

8. *Sodium nitrite solution* gives with traces of morphine a yellow coloration, which becomes orange on the addition of sodium hydroxide (Wieland and Kappelmaier[3]). If *acidified* nitrite solution is used, and the liquid rendered alkaline with concentrated potassium hydroxide solution, the colour varies according to the concentration, from pale pink to deep ruby-red. The colour disappears on the addition of acid, but returns again when alkali is added.

9. A solution of 0·5 grm. of **selenious acid** (H_2SeO_3) in 100 grms. of concentrated sulphuric acid gives, on contact with morphine, a blue coloration which, after a short time, becomes permanently bluish-green to olive-green. On heating the liquid, the colour becomes brown; the test is capable of detecting 0·005 mgrm. (Mecke[4]).

10. On heating a solution of morphine in pure concentrated *sulphuric acid* with a small amount of *sodium* or *potassium arsenate* until it becomes red, the liquid, when cautiously diluted with water, after cooling, becomes reddish to red, and on the further addition of water, green. On then shaking it with chloroform or ether it changes to a fine bluish-violet colour, whilst the organic solvent becomes reddish-violet (Tattersall,[5] Donath).

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[1] *Ann. d. Chem.*, **128**, 305; *Arch. d. Pharm.* [3] **6, 231.**

[2] Dragendorff, *Beitrage zur gerichtlichen Chemie einzelner organischer Gifte* (Petrograd, 1872), p. 124.

[3] *Ann. d. Chem.*, **382**, 306 (1911).

[4] *Zeitsch. öffentl. Chem.*, **5**, 351 (1899).

[5] *Chem. News*, **41**, 63.

11. A freshly-prepared solution of 0·1 grm. of **ammonium molybdate** in 1 c.c. of concentrated **sulphuric acid** (Fröhde's reagent,[1] modified by Buckingham[2]) gives highly characteristic colorations with morphine, a solid morphine salt, or a drop of a solution of a morphine salt, even in the presence of the most minute traces of the alkaloid. If a few drops of the solution are placed on a porcelain surface, and a spicule of morphine added and crushed with a glass rod, a deep violet coloration is immediately obtained. This gradually changes to olive green, whilst the margin of the sulphuric acid becomes a fine dark blue. On adding a drop of a dilute solution of a morphine salt to the solution a deep blue ring, which sometimes has a violet margin, is immediately obtained, and subsequently the drop in the middle, and gradually the whole liquid, changes to a fine blue.[3] The reaction is extremely sensitive (Kauzmann and Dragendorff were able to detect as little as 0·005 mgrm. of anhydrous morphine sulphate by its means), but is not of itself conclusive, since other organic substances (phloridzine, salicine, digitaline, etc.) produce similar colorations. It should also be noted that the reaction must take place immediately, since the reagent becomes blue when allowed to stand for some time exposed to the air, owing to the action of dust. On the addition of water the liquid, which has been rendered blue by morphine, becomes very pale yellow, almost colourless. (Distinction from salicine, which then yields a reddish fluid.)

12. On bringing an intimate mixture of 1 part of morphine with about 6 to 8 parts of *sugar* into contact with a few drops of *concentrated sulphuric acid* on a porcelain tile, a pink to purple-red coloration, according to the amount of morphine, is obtained. The coloration lasts for a considerable time, but gradually changes through absorption of water into bluish-violet, then into dirty bluish-green, and finally into dirty brownish-yellow.

The reaction is obtained distinctly with 0·1 to 0·01 mgrm. of morphine. In the case of dilute solutions of morphine salts, a drop of the liquid should be treated with as much sugar as it will dissolve, a drop of concentrated sulphuric acid placed beside it, and the edges of the drops brought into contact by inclining the tile (R. Schneider[4]).

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[1] *Zeitsch. anal. Chem.*, **5**, 214.

[2] *Ibid.*, **13**, 234.

[3] With regard to the spectroscopic phenomena of these colour reactions, *cf.* Dragendorff, *Zeitsch. anal. Chem.*, **35**, 758 (1896).

[4] *Zeitsch. anal. Chem.*, **12**, 218.

The addition of, at most, three drops of bromine water increases the sensitiveness of the reaction (Weppen[1]).

13. On evaporating morphine or its sulphuric or hydrochloric acid salt with a few drops of *formaldehyde solution* nearly to dryness in a white porcelain dish, adding a drop of *stannous chloride solution,* while the liquid still has an odour of formaldehyde, and rubbing the residue with a glass rod, there is at first no material alteration. On continuing the drying, however, a fine violet spot appears and gradually increases in intensity, until finally it shows a coloration almost bordering on black, even in the presence of minute traces of a morphine salt. The reaction cannot be produced with alkaline solutions of morphine (C. Reichard[2]).

14. Morphine *dissolves* in a freshly-prepared mixture of two to three drops of 40 per cent. **formaldehyde solution** and 3 c.c. of *concentrated sulphuric acid* to form a solution which is violet at first, but slowly changes to bluish-violet, blue, bluish-green, and green. The sensitiveness of the reaction is 0·001 mgrm. (Marquis[3]).

15. On treating morphine with four or five drops of a freshly-prepared solution of two drops of *furfural* and 10 c.c. of *concentrated sulphuric acid* the mixture becomes bright red, the colour changing to olive-green on heating (Brunner and Strzyzowski[4]). According to N. Wender,[5] however, a transient violet coloration is produced when the liquid is heated.

16. On dissolving a small amount of morphine in about 1 to 1·5 c.c. of *concentrated hydrochloric acid*, adding a drop of *concentrated sulphuric acid*, and heating the liquid in an oil bath at 100°–120° C. (or on the water bath) until all hydrochloric acid has volatilised, a purple-red residue is obtained. On again treating this with a small quantity of hydrochloric acid, then adding a cold saturated solution of sodium hydrogen carbonate until the liquid has a neutral or only slightly acid reaction, and lastly introducing a drop of an *alcoholic solution of iodine,* the liquid assumes an emerald-green coloration. On now shaking the liquid with ether the substance causing the green coloration (apomorphine) is dissolved by the ether, and a fine violet-red ethereal layer is obtained (Pellagr[6]). Codeine gives the same reaction.

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[1] *Zeitsch. anal. Chem.*, **13**, 455. With regard to the spectroscopic behaviour, *cf. Ibid.*, 35, 758 (1896).

[2] *Ibid.*, **46**, 72 (1907).

[3] *Ibid.*, **40**, 61 (1901).

[4] *Ibid.*, **38**, 459 (1899).

[5] *Ibid.*, **42**, 328 (1903).

[6] *Ibid.*, **17**, 373 (1878).

17. On treating a solution of a morphine salt with a large excess of alkali hydroxide, and adding *iodine-potassium iodide solution*, the first addition produces only a yellow coloration (so long as the iodine is still in combination with the alkali). On the further addition of iodine solution, as gradually as possible, the liquid assumes a grass-green coloration, which is particularly distinct on dilution with water. Not until a large quantity of iodine has been added does an insoluble compound separate. If, however, the morphine solution was neutral or slightly acid, the dark brown compound of periodide and hydriodic acid is immediately precipitated (C. Kippenberger [1]). According to Dragendorff this precipitate is formed even in a liquid diluted to 1 : 5000.

18. When **iodic acid** or **sodium iodate and sulphuric acid** is brought into contact with a solution of morphine or of a morphine salt, iodine is precipitated. If the solution was aqueous and concentrated, a brown precipitate is produced, but if alkaline or dilute, the liquid becomes brown or yellowish-brown. If starch paste is added to the liquid before, or immediately after, the addition of the iodic acid, the sensitiveness of the reaction is considerably increased, since the blue coloration of the resulting starch is visible in far greater dilution than the brown colour of the iodine. The reaction is most sensitive when the iodic acid solution is treated with a little starch paste, and the morphine salt introduced in the solid condition. It need hardly be mentioned that the sensitiveness of the reaction may be intensified by extracting the liberated iodine from the aqueous solution by means of carbon bisulphide.

Inasmuch as other nitrogenous compounds (albumin, casein, fibrin, etc.) also reduce iodic acid, the mere separation of iodine has only a relative value. If, however, *ammonia* is added after the addition of the iodic acid, the liquid will remain colourless when the precipitation of iodine was due to other substances, whilst in the case of morphine a much more intense coloration is produced (Lefort [2]).

19. *Neutral ferric chloride* gives a fine dark blue coloration with *concentrated* neutral solutions of morphine salts. Free acids cause the coloration to disappear; excess of ferric chloride has also an influence on its sensitiveness. The addition of 0·2 c.c. of a 5 per cent. solution of ferric chloride is sufficient for the precipitation of 0·01

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[1] *Zeitsch. anal. Chem.*, **35**, 415 (1896).

[2] *Ibid.*, **1**, 134. The reactions with *silver nitrate* (Horsley, *Ibid.*, **7**, 485) and *copper oxide ammonia solution* (Nadler, *Ibid.*, **13**, 235), which are applicable to the detection of morphine, also depend upon the reducing power of the alkaloid.

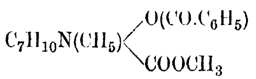
grm. of morphine hydrochloride dissolved in 100 to 200 c.c. of water. Using these proportions Dragendorff obtained the reaction with solutions containing as little as 1 part of morphine salt in 1000 to 1500 parts of water. If animal or vegetable extractive substances or acetates are present, the coloration becomes impure and less distinct. The sensitiveness, of the reaction is increased by adding a little potassium ferricyanide, because this compound is reduced to potassium ferrocyanide, and causes the formation of Prussian blue, while the morphine is oxidised to oxydimorphine (Kiefer, O. Hesse). It is obvious that the reaction thus modified is only distinctive of morphine in the absence of other substances with a reducing action.

20. Of the *general precipitation reagents*, gold chloride, potassium bismuth iodide, and phosphomolybdic acid give a turbidity or precipitate with morphine sulphate, even in a dilution of 1 : 5000. The phosphomolybdic precipitate becomes dark blue with concentrated sulphuric acid, and, on heating, turns dark brown and reduces iodic acid (*cf.* 18). Potassium mercuric iodide, and potassium cadmium iodide produce precipitates in solutions of 1 : 1000. Tannic acid gives only a slight turbidity at this concentration, but at a higher concentration produces a white precipitate soluble in acids. In a dilution of 1 : 100 picric acid produces a copious yellow precipitate, which dissolves on the addition of water. Mercuric chloride gives a crystalline precipitate, and platinum chloride a slight precipitate in solutions diluted to the same extent.

SEC. 214.

2. Cocaine, $C_{17}H_{21}NO_4$.

Methyl ester of benzoylecgonine,



$$C_7H_{10}N(CH_5)\begin{cases} O(CO.C_6H_5) \\ COOCH_3 \end{cases}$$

1. *Cocaine* occurs in association with several other allied alkaloids in the leaves of the South American tree *Erythroxylon coca.* It crystallises from an alcoholic solution treated with water in colourless transparent rods, melts at 98°, and solidifies, on cooling, to a transparent, amorphous mass, which, after some time, becomes white and crystalline. Its taste is bitter, followed by a sensation of cold; it produces local anæsthesia, is stupefying, and enlarges the pupil of the eye. According to W. Müller,[1] it dissolves in 563 parts of water at about 20°, is readily soluble in alcohol, in 42·2 parts of petroleum

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[1] *Apothekerztg.*, 18, 208 and 266 (1903).

spirit, in 2·9 parts of ether saturated with water, in 1·7 parts of ethyl acetate, and (according to J. Schindelmeiser [1]) in 5·4 parts of carbon tetrachloride. It rotates a beam of polarised light to the left: $[\alpha]_D = -16{\cdot}4$ (in 10 to 20 per cent. solution in chloroform). The solutions have an acid reaction.

2. Cocaine dissolves readily in dilute acids, while it combines with them to form *salts*. Cocaine hydrochloride is easily obtained in the form of crystals, which are stable in the air, have a very bitter taste, and a neutral reaction, and are soluble in water, alcohol, and chloroform, but insoluble in ether. On shaking a solution of cocaine in excess of dilute hydrochloric acid with ether, chloroform, petroleum spirit, or benzene, the cocaine is not dissolved by these solvents, but can be extracted by amyl alcohol.

3. *Potassium or sodium hydroxide* produces in solutions of cocaine salts a white precipitate which gradually dissolves in excess of the precipitant. In like manner, *ammonia* produces a precipitate, which, however, is more soluble in excess of the reagent. Ether extracts the cocaine from the ammoniacal solution on shaking, and petroleum spirit also extracts it readily. When the petroleum spirit extract is allowed to evaporate spontaneously the cocaine is left in the form of fine needles.

4. *Potassium or sodium carbonate*, added to solutions of cocaine salts, produces amorphous white precipitates, which are insoluble in excess of the precipitant; they become crystalline on standing for some time. On shaking the liquid containing the precipitate with ether, the cocaine is extracted.

5. *Potassium or sodium hydrogen carbonate* produces no precipitate in solutions of cocaine salts in the cold. When the liquid is heated to boiling point a precipitate is formed, but re-dissolves on cooling.

6. If cocaine is heated with *concentrated hydrochloric acid*, in a *glass tube closed by fusion*, for 2 to 3 hours, in a water bath it is decomposed into *benzoic acid*, *ecgonine hydrochloride*, and *methyl alcohol* (Losson [2]). The benzoic acid separates, on cooling, in crystals, if its amount is not too small.

7. When cocaine is heated in a test-tube with **concentrated sulphuric acid** the same decomposition is effected. After cooling, needles of sublimed benzoic acid will be found in the upper part of the test-tube, unless too small a quantity was used. If alcohol was

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[1] *Chem. Zeit.*, **25**, 129 (1901); *Zeitsch. anal. Chem.*, **41**, 632.

[2] *Ann. d. Chem.*, **133**, 351.

added prior to the heating, the characteristic odour of the ethyl ester of benzoic acid will be observed. This odour is also produced when cocaine is heated with alcoholic potassium hydroxide solution.

8. Cocaine dissolves in *concentrated sulphuric acid* to form a colourless liquid, in which no coloration is produced on the addition of a small amount of nitric acid, even after heating the sulphuric acid solution to about 150°. Nor does sulphuric acid containing molybdic acid or sugar produce liquids with characteristic colorations. (Distinction from morphine.)

9. Cocaine does not precipitate iodine from a dilute solution of *iodic acid.* (Distinction from morphine.)

10. When cocaine is dissolved in 0·5 to 1 c.c. of *concentrated sulphuric acid,* a quantity of *potassium* or *sodium iodate* equal to about three times that of the cocaine added, and the mixture gently heated on the water bath, the liquid first becomes yellow, and then shows pale green streaks. On continuing the heating the whole liquid becomes grass-green, then brown, and finally iodine vapour escapes. Vitali[1] also observed blue and violet colorations; the same result was also obtained by Dragendorff and Gadamer, who used somewhat more iodate (a small granule with a trace of cocaine).

11. On treating a solution of 0·05 grm. of cocaine hydrochloride in 5 c.c. of water, drop by drop, with 5 per cent. **chromic acid solution,** or 10 per cent. **potassium chromate solution,** or 7·5 per cent. **potassium dichromate solution,** an orange-coloured precipitate of cocaine chromate is obtained; this re-dissolves immediately, but is re-precipitated on the addition of 1 c.c. of concentrated hydrochloric acid.

12. When a few drops of a cocaine solution are mixed with 2 to 3 c.c. of chlorine water, and a few drops of a 5 per cent. solution of *palladous chloride* are added, a fine red precipitate is produced (Greitherr).

13. *Stannous chloride* produces a compact white caseous precipitate, soluble in nitric acid, in concentrated solutions of cocaine salts (Noemann).

14. When approximately equal parts of cocaine and *mercurous chloride* are ground up together, and the mixture moistened by breathing upon it, it turns black, owing to the separation of metallic mercury (Schell,[2] Schneider[3]).

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[1] *Zeitsch. anal. Chem.*, **30**, 265 (1891).

[2] *Ibid.*, **30**, 264 (1891).

[3] *Ibid.*, **42**, 200 (1903).

15. On treating a solution of a cocaine salt with *mercuric chloride* there is produced a white precipitate, which is soluble in hydrochloric acid, ammonium chloride solution, and alcohol (Niemann).

16. *Tannic acid* produces a precipitate in solutions of cocaine which have been treated with hydrochloric acid. The yellowish precipitate which first separates becomes agglomerated into a resin-like mass on standing for some time, and immediately when shaken (Niemann).

17. The *general precipitation reagents* will detect the following amounts of cocaine hydrochloride in aqueous solution: Potassium mercuric iodide, 1 : 160,000; iodine in potassium iodide solution, 1 : 100,000; phosphomolybdic acid, 1 : 50,000; and picric acid, 1 : 1400 to 1500.[1]

18. Nearly all the above-mentioned reactions are not very characteristic. Hence, as a rule, a physiological test must also be used for the detection of cocaine. The **microchemical reactions** will also be found of value. Of these mention may be made of the following: Auric chloride produces forked and crossed needles in dilute solutions (1 : 1000), and yellow extended dendritic and **H**-shaped crystals in concentrated solutions. The limit of sensitiveness is 0·00008 mgrm. (Behrens). With *β-naphthalene sulphonic acid* colourless thin prisms, usually extended hexagons, are obtained in a few minutes. This is less sensitive (A. Grutterink [2]). On introducing a drop of a 1 per cent. *potassium permanganate solution* into the middle of a drop of a cocaine solution, and observing it without a cover-glass under a low magnification, there will be seen after five minutes at the margin of the liquid small finger-shaped or hand-shaped formations, together with numerous globules, which frequently unite with several others. The limit of sensitiveness is 0·1 mgrm. (Giesel,[3] E. Senft [4]).

SEC. 215.

Summary and Remarks on Non-Volatile Alkaloids (Group I.).

Morphine and cocaine may be distinguished by many reactions, of which those given in Sec. 213, 7, 9, 10, 11, 12, 16, 18, and 19 are particularly important for morphine, and those in Sec. 214, 6, 7, 10, and 14 for cocaine. Both alkaloids may be separated by rendering the solution of their salts just alkaline with ammonia, and shaking it with petroleum spirit, which will extract the cocaine and leave the morphine. On evaporating the petroleum spirit, a residue of morphine is left.

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[1] Colour reactions for cocaine have also been described by C. Reichard (*Chemikerztg.*, **28**, 299 (1904); *Pharm. Ztg.*, **51**, 168, 591 (1906).

[2] *Zeitsch. anal. Chem.*, **51**, 208 (1912).

[3] *Ibid.*, **47**, 447 (1908).

Zeitsch. Unters. Nahr. Genuss., **7**, 345 (1904)

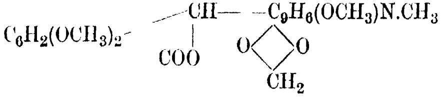
Second Group.

Non-volatile alkaloids which are precipitated by potassium hydroxide from solutions of their salts, and are not re-dissolved on the addition of a considerable excess of the precipitant, and which are precipitated by sodium hydrogen carbonate from acid solutions, if these are not more dilute than 1 : 100.

Narcotine, Quinine, Cinchonine.

Sec. 216.

1. Narcotine, $C_{22}H_{23}NO_7$.



1. *Narcotine* occurs, together with morphine, etc. (*cf.* Sec. 213, 1), in opium. Crystallised narcotine is usually in the form of colourless, lustrous, straight, rhombic rods, or (when precipitated by alkalis) a loose white crystalline powder. It melts at 176°. The solid alkaloid is tasteless, and is much less poisonous than morphine. It is soluble in 10,000 parts of water at 15°, in 5000 parts of petroleum spirit, in 415 parts of amyl alcohol, in 190 parts of alcohol, in 170 parts of ether, in 31 parts of ethyl acetate, in 22 parts of benzene, and in 4 parts of chloroform (M. Scholtz,[1] Dieterich[2]). Litmus and other vegetable colouring matters are not changed by solutions of narcotine. The free alkaloid rotates a beam of polarised light to the left: $[\alpha]_D = -207{\cdot}4°$ (in chloroform solution). The solutions of the salts have a dextro-rotation.

2. Narcotine is a weak base. It dissolves readily in acids, and combines with them to form *salts*. These always show an acid reaction. The salts containing weak acids are decomposed on treatment with much water, and also on evaporating their solutions, if the acids are volatile. Most of them are uncrystallisable and are

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[1] *Arch. d. Pharm.*, **250**, 418 (1912).

[2] *Pharm. Zentralh.*, **28**, 481 (1887).

soluble in water, alcohol, and ether ; they have a bitter taste. Narcotine is insoluble in water slightly acidified with acetic acid, *i.e.* containing not more than 3 or 4 drops of the acid in 2 c.c. On shaking solutions of narcotine salts with chloroform the narcotine is extracted by the latter, even when the solutions contain free acid (Dragendorff). Ether has an analogous although weaker action (R. Otto [1]). Benzene, amyl alcohol, and petroleum spirit do not extract narcotine from acid solutions.

3. *Alkali hydroxides*, *carbonates*, and *hydrogen carbonates* precipitate narcotine immediately from solutions of narcotine salts as a white powder, which may be seen, under a magnification of 100 diameters, to consist of an aggregate of small needle-shaped crystals. The precipitate is insoluble in excess of the precipitant. On treating a solution of a narcotine salt with ammonia, and then shaking it with not too small a quantity of ether, two clear layers are obtained, the separated alkaloid having been dissolved by the ether. When a drop of the ethereal solution is allowed to evaporate on a glass slide, and the residue examined under a magnification of 100 diameters, it will be seen to consist of well-defined long crystals, some of which are pointed.

4. Hot *nitric acid* of sp. gr. 1·4 dissolves narcotine to form a reddish-yellow solution, while nitrous acid fumes are evolved. When the solution is heated there is a further evolution of nitrous acid fumes, and the liquid becomes yellow.

5. **Concentrated sulphuric acid** dissolves narcotine to form a solution, the colour of which is greenish-yellow, but soon becomes pure yellow ; after some days the liquid assumes a raspberry-red coloration (Dragendorff). When carefully heated in a porcelain basin the solution becomes first orange-yellow, then shows bluish-violet or sometimes purple-blue streaks extending from the margins, and finally an impure reddish-violet coloration is produced at the temperature at which the sulphuric acid begins to escape. If the heating was stopped prior to this point, the solution, on cooling, slowly assumes a delicate cherry-red coloration. The blue coloration is still very distinct when the sulphuric acid contains 1 part in 2000 of the alkaloid ; in the presence of a smaller proportion a soft crimson coloration is obtained instead of the blue coloration (A. Husemann). The red and subsequent violet colour of the sulphuric acid solution is also produced when the narcotine is dissolved in dilute (1 : 5) sulphuric acid, the colourless solution evaporated *very*

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[1] *Arch. d. Pharm.*, 234, 317.

gradually over a small flame, and the heating of the residue continued very cautiously. This is a particularly sensitive method of applying the test (Dragendorff). On treating the liquid which has become violet with a sufficient quantity of alcoholic potassium hydroxide solution there is obtained an orange-red coloration, which becomes yellow on the addition of water (Arnold [1]).

6. On adding a very small quantity (a trace to a drop) of dilute *nitric acid* to a solution of narcotine in concentrated sulphuric acid prepared in the cold, the liquid becomes at first almost brown, but soon changes to red, which becomes increasingly intense (Couerbe). According to Dragendorff the sensitiveness of the reaction increases when the solution of narcotine in sulphuric acid is allowed to stand for one or two hours prior to the addition of the nitric acid. This reaction is produced when narcotine is dissolved in **Erdmann's reagent.** The latter is prepared by mixing 6 drops of nitric acid of sp. gr. 1·25 with 100 c.c. of water, and causing 10 drops of this solution to fall on to 20 grms. of pure concentrated sulphuric acid.

7. The addition of *sodium hypochlorite* to a solution of narcotine in *concentrated sulphuric acid*, which has been heated to 150°, causes a crimson coloration to appear (A. Husemann).

8. If a solution of narcotine in *concentrated sulphuric acid* is heated until a red coloration appears (to about 150°), and then cooled and treated with *ferric chloride*, the portions of the liquid which are in immediate contact with the added drops of ferric chloride solution soon appear red, with more or less pronounced pale violet edges; after 10 to 15 minutes a fairly stable cherry-red coloration is produced (A. Husemann).[2]

9. On treating a solution of a narcotine salt with *chlorine water* it becomes yellow with a greenish tint, and on then adding ammonia an intensely coloured yellowish-red liquid is obtained.

10. When narcotine or one of its compounds is dissolved in excess of dilute sulphuric acid, and the solution treated with a little powdered *manganese dioxide*, boiled for a few minutes, and filtered, a filtrate is obtained from which narcotine is not precipitated by ammonia. The alkaloid has been converted through the absorption of oxygen into opianic acid and cotarnine (Wöhler [3]).

11. *Mecke's reagent* (Sec. 213, 9) gives a greenish-blue, and subsequently a cherry-red, coloration with narcotine in the cold.

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[1] *Arch. d. Pharm.*, **220**, 563 (1882).
[2] *Zeitsch. anal. Chem.*, **3**, 152.
[3] *Ann. d. Chem.*, **50**, 1.

12. ***Fröhde's reagent*** (containing 0·005 grm. of sodium molybdate in 1 c.c. of sulphuric acid) dissolves narcotine to form a green solution. If the solution contains 0·1 grm. of sodium molybdate in 1 c.c. of sulphuric acid, the green colour soon changes into a fine cherry-red coloration (Dragendorff).

13. A solution of **ammonium vanadate in concentrated sulphuric acid** (1 : 100 to 200) dissolves narcotine to form a solution which is first vermilion red, then reddish-brown, and finally a gradually intensifying carmine-red (Mandelin).

14. On heating 2 to 10 mgrms. of narcotine with 20 drops of pure *concentrated sulphuric acid* and one or two drops of a 1 per cent. solution of *cane sugar* for a minute on the boiling water bath, with continual stirring, the greenish-yellow solution first formed changes first to yellow, then to brown, and finally to deep bluish-violet. The colour gradually intensifies on standing, and remains unchanged for several hours. If an aqueous solution of *furfural* is used, instead of the cane sugar solution, an intense deep blue coloration is produced on heating, and this gradually changes to green when the liquid is allowed to stand (A. Wangerin [1]).

15. *Tannic acid* does not produce a precipitate, or at most only a turbidity, in solutions of narcotine salts. On adding a drop of hydrochloric acid to the solution a precipitate is formed. This dissolves when the liquid is heated, but reappears when it cools. The precipitate is only slightly soluble in hydrochloric acid.

16. Of the *generăl precipitation reagents* the most sensitive for narcotine are iodine in potassium iodide solution (1 : 50,000), potassium mercuric iodide (1 : 50,000), potassium bismuth iodide, and phosphomolybdic acid (Dragendorff [2]).

SEC. 217.

2. Quinine, $C_{20}H_{24}N_2O_2$.

Methoxycinchonine, $C_9H_5(OCH_3)N—CH(OH)—C_7H_{11}(CH : CH_2)N$.

1. *Quinine* occurs in association with cinchonine and about 20 other bases in genuine cinchona bark derived from various species of the family *cinchona*. Crystallised quinine, $C_{20}H_{24}N_2O_2.3H_2O$, is known either in the form of fine lustrous silken needles, often united into bunches, and readily disintegrating on exposure to the air, or as a

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[1] *Zeitsch. anal. Chem.*, **46**, 257 (1907).

[2] Colour reactions for narcotine have also been described by C. Reichard (*Pharm. Zentralh.*, **48**, 44 (107); *Zeitsch. anal. Chem.*, **49**, 780).

bulky white powder. Quinine free from water of crystallisation can also be obtained in lustrous silken acicular crystals. Quinine, containing water of crystallisation, is soluble in 1650 parts of water, and the anhydrous alkaloid in 1960 parts at 15°, and more readily in hot water (Hesse). It dissolves in 22·6 parts of ether, in 1·9 parts of chloroform, and in 1·1 parts of alcohol (Regnauld); it dissolves with difficulty in benzene, and with very great difficulty in petroleum spirit. It is lævo-rotatory: $[\alpha]_D = -158{\cdot}2°$ (for the anhydrous base dissolved in absolute alcohol). It is only slightly poisonous, and has a bitter taste; its solutions show an alkaline reaction.[1] Crystallised quinine loses its water at 100°; it melts at 57°, and resolidifies after it has parted with its water.

2. Acids neutralise quinine completely. Two series of *salts* are formed, containing respectively 1 and 2 molecules of water to 1 molecule of quinine (formerly termed neutral and acid salts). Most of the mono-acid salts are crystallisable, dissolve with difficulty in cold, but more readily in hot, water, and also in alcohol, and have a very bitter taste.

The di-acid salts dissolve very readily in water. The solutions which contain oxygenated acids, and especially those in which sulphuric acid predominates, show a **bluish fluorescence.** If a cone of light is introduced into them by means of a lens from the side or from above it appears blue, even in the case of very dilute solutions (A. Flückiger).

3. *Potassium and sodium hydroxide, ammonia,* and the *alkali carbonates* precipitate from solutions of quinine salts which are not too dilute, quinine containing water of crystallisation as a bulky white powder, which, when examined under the microscope immediately after the precipitation, appears amorphous and opaque, but after some time forms an aggregate of needle-shaped crystals. The precipitate is only slightly soluble in excess of potassium or sodium hydroxide solution (less readily than in water), and is less soluble in potassium hydroxide than in sodium hydroxide solution F. Sestini), but more soluble in ammonia solution. According to W. Duncan,[2] however, the solubility of quinine in ammonia solution is only apparent, and it soon separates again in crystals on standing. It is also only soluble to a slight extent in potassium or sodium carbonate solutions. Ammonium chloride increases the solubility

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[1] For its behaviour towards different indicators, *cf.* A. H. Allen, *Analyst,* **21** 85, and J. Larrouturron, *Zeitsch. anal. Chem.,* **49,** 132.

[2] *Zeitsch. anal. Chem.,* **49,** 391 (1909).

in water. If a solution of a quinine salt is treated with ammonia and shaken with ether (containing about 2 per cent. of alcohol) the precipitate disappears, and two clear layers of liquid are formed. (*Essential distinction from cinchonine*, which in this way may be readily detected in the presence of quinine, and separated therefrom.)

4. If *potassium hydroxide* is fused after the addition of a drop of water, an alcoholic solution of quinine added to the still warm mass, and the mixture carefully heated to evaporate the alcohol, the mass assumes a fine green coloration. (Essential distinction from nearly all other alkaloids, but not from quinidine.) Cinchonine, cinchonidine, and cocaine show a similar but not the same coloration (W. Lenz).

5. *Sodium hydrogen carbonate* produces a white precipitate both in neutral and in acid solutions. If acid solutions are diluted to such an extent that they contain 1 part of quinine to 100 parts of liquid, the precipitate is formed immediately; in the proportion of 1 : 150 it separates after 1 to 2 hours in the form of distinct needles united in groups. The precipitate is not completely insoluble in the precipitant, and hence the less the excess of the latter the more complete is the separation; the precipitate contains carbonic acid.

6. Quinine is dissolved by *concentrated nitric acid* to form a colourless solution, which has a bluish fluorescence, and, when heated, becomes yellow.

7. *Concentrated sulphuric acid* dissolves pure quinine or pure quinine compounds, forming a colourless or slightly yellow solution; on warming the liquid the yellow coloration increases in intensity, and on continuing the heating the solution becomes brown. Sulphuric acid containing nitric acid (Erdmann's reagent, *cf.* Sec. 216, 6) dissolves quinine to form a colourless or faint yellow solution.

8. A solution of *ammonium vanadate* in *concentrated sulphuric acid* (1 : 100) when treated with quinine soon becomes brownish-green, but after about 5 minutes the colour changes to a permanent pure green.

9. When a solution of a quinine salt is treated with strong *chlorine water* (about $\frac{1}{5}$ volume) little if any coloration is produced, but on then adding excess of *ammonia solution* an intense emerald-green solution is obtained. This characteristic reaction (*thalleioquin reaction*) is obtained in a dilution of 1 : 2500, or, according to Flückiger,[1] even in a dilution of 1 : 4000 to 1 : 5000, if one-tenth volume of chlorine water is added to the solution, without shaking,

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[1] *Zeitsch. anal. Chem.*, **11, 318.**

and then a few drops of ammonia solution, and the test-tube gently shaken.

If *bromine water* is used instead of chlorine water, the sensitiveness of the reaction is still greater, but an excess or deficiency of bromine interferes with the result to a greater extent than in the case of chlorine. Léger[1] recommends the addition of 1 c.c. of about 0·05 per cent. bromine water to 10 c.c. of a quinine solution, the reagent being prepared by mixing equal parts of a saturated aqueous solution of bromine and of water. If a layer of ammonia solution is poured on to the mixture containing the quinine there is immediately produced at the zone of contact a green ring, and below it a red ring, while the liquid beneath remains yellow. The sensitiveness of this reaction can be increased to 1 : 20,000 by mixing 10 c.c. of a solution of quinine with a drop of saturated bromine water, and carefully allowing a drop of ammonia solution to fall on to the surface; this causes a green ring about 1 cm. in depth to be formed over the colourless liquid.[2]

Morphine inhibits the thalleioquin reaction (Stuart[3]), as do also caffeine and antipyrine, the former when present in the proportion of 1·5 parts and the latter of 3 parts to 1 part of quinine.[4] If pyramidone is present, even in small amount, with the quinine the thalleioquin reaction is red instead of green.[5]

10. If in the thalleioquin reaction a little **potassium ferrocyanide solution** is added after the chlorine water, and then a few drops of ammonia solution (or another alkali), the liquid becomes a fine deep red (**erythroquin reaction**). The colour soon changes to dirty brown. On adding an acid, preferably acetic acid, to the red liquid, the colour disappears, but is reproduced on the cautious addition of ammonia solution (O. Livonius, A. Vogel[6]). J. Abensour[7] treats 10 c.c. of the slightly acidified aqueous solution of quinine with one drop each of semi-saturated bromine water, 10 per cent. potassium ferrocyanide solution, and 10 per cent. ammonia solution. On shaking this mixture with chloroform a pink to red coloration is obtained, according to the quantity of quinine.

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[1] *Zeitch. anal. Chem.*, **44**, 578 (1905).

[2] Polacci (*Zeitsch. anal. Chem.*, **40**, 60 (1901)) describes a modification of the thalleioquin reaction, in which lead peroxide is used instead of chlorine or bromine water.

[3] *Pharm. Zentralh.*, **23**, 312 (1882).

[4] A. Belohoubek and Sedlecky, *Zeitsch. anal. Chem.*, **35**, 236 (1896).

[5] C. Mannich and L. Schwedes, *Ibid.*, **52**, 64 (1913).

[6] *Ibid.*, **23**, 78 (1884).

[7] *Ibid.*, **49**, 133 (1910).

11. On dissolving quinine in a little acetic acid, and adding alcohol and then alcoholic **iodine solution** (prepared by dissolving 1 part of iodine in 1 part of 50 per cent. hydriodic acid, 50 parts of 70 per cent. alcohol, and 0·8 part of sulphuric acid), in sufficient quantity to render the liquid brownish-yellow, there separates, after a short time, an acid periodide-quinine iodide sulphate (*herapathite*), $4C_{20}H_{24}N_2O_2.3H_2SO_4.2HI.I_4$. According to the conditions this appears in the liquid as a crystalline blackish powder, or as large hexagonal or octagonal crystalline flakes, which by transmitted light appear only pale olive-green, but by reflected light are bright green, with a metallic lustre. In polarised light they appear green or red, according to the position of the axis (Herapath[1]). *This is a very characteristic reaction, which, when observed with the polarisation microscope, is also very sensitive.*

12. *Tannic acid* produces a white precipitate in aqueous solutions of quinine salts, even when very dilute. The precipitate is caseous and agglomerates when heated. It is soluble in acetic acid and in a small quantity of hydrochloric acid, but is precipitated on the addition of a further quantity of that acid.

13. The *general precipitation reagents* behave as follows: Iodine in potassium iodide solution gives a reaction with solutions containing 1 : 200,000; potassium bismuth iodide with one containing 1 : 150,000; and potassium mercuric iodide with one of 1 : 100,000. Phosphomolybdic acid, phosphotungstic acid, and picric acid are also sensitive reagents.

14. With regard to the *microchemical reactions* of quinine, see the communications of A. Grutterink.[2]

SEC. 218.

3. **Cinchonine,** $C_{19}H_{22}N_2O$.

$C_9H_6N—CH(OH)—C_7H_{11}(CH : CH_2)N$.

1. *Cinchonine*, which occurs with quinine and other bases in true cinchona bark, is known either as colourless lustrous rhombic crystals, or fine white needles, or (when obtained by precipitation from concentrated solutions) as a bulky powder. It is tasteless at first, but subsequently develops a bitter flavour. One part of cinchonine dissolves in 3670 parts of water at 20°, and more readily

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[1] *Phil. Mag.*, (4) **3**, 161; **4**, 186; *J. prakt. Chem.*, **61**, 87 (1864).

[2] *Zeitsch. anal. Chem.*, **51**, 215 (1912).

in boiling water, in 371 parts of ether at 20° (according to other authorities a larger quantity is required), and in 126 parts of alcohol (78 per cent. by weight) at 20° (Hesse[1]). In the case of chloroform absolutely free from alcohol 356 parts are required for the solution at 17°, whilst mixtures of chloroform and alcohol dissolve cinchonine much more readily than chloroform, and, under some conditions, than pure alcohol (Oudemans[2]). Benzene dissolves amorphous cinchonine readily in the cold, but the crystalline alkaloid with more difficulty. On heating the liquid, the crystalline cinchonine is also dissolved, but separates again almost completely when the solution cools. Petroleum spirit dissolves only slight traces of freshly precipitated amorphous cinchonine (Dragendorff). The solutions have a bitter taste and an alkaline reaction. Cinchonine is dextro-rotatory; in alcoholic solution it has $[\alpha]_{\mathrm{D}} = +223^\circ$, and in chloroform solution $+213^\circ$ (Oudemans[3]).

2. On *heating* cinchonine *carefully* it begins to sublime below its melting point at about 200°, emitting a characteristic odour, and producing white fumes. When heated in a current of hydrogen it forms long lustrous prisms (Hlasiwetz). When rapidly heated it melts at 268·8°, and at a considerably lower temperature when slowly heated (owing to incipient decomposition).

3. Cinchonine is a strong base; it liberates ammonia from boiling solutions of ammonium salts (Hesse[4]). Like quinine, it combines with acids to form two series of *salts*. The salts have a bitter taste; most of them are crystallisable; as a rule they are more soluble than the corresponding quinine salts. They are insoluble, or nearly so, in ether and chloroform. The solutions of the salts do not show fluorescence. (Essential distinction from quinine salts.)

4. *Potassium and sodium hydroxides, ammonia and alkali carbonates* precipitate cinchonine as a bulky white powder from solutions of its salts. The precipitate is insoluble in excess of the precipitant. If the solution was concentrated the precipitate appears only indistinctly crystalline, even under a magnification of 200 diameters, but if it was so dilute that the precipitate only formed after standing for some hours, it is seen under the microscope to consist of needles united into star-formed bunches.

5. When cinchonine is fused with *potassium hydroxide*, as was described in the case of quinine (Sec. 217, 4), the projecting points

[1] *Ann. d. Chem.*, **122**, 226.
[2] *Ibid.*, **166**, 75.
[3] *Ibid.*, **182**, 44.
[4] *Ibid.*, **166**, 257.

of the solidified fused mass become first reddish-brown to violet-blue, and the margins grey, whilst subsequently the mass becomes bluish-green and develops a somewhat penetrating odour (W. Lenz).

6. *Sodium or potassium hydroxide*, added to neutral or acidified solutions of cinchonine salts, precipitates *cinchonine* in the form described in 4, but not so completely as do the corresponding carbonates. Even in the case of solutions which contain 1 part of cinchonine to 201 parts of water+acid, the precipitate is formed immediately; its amount increases on standing.

7. Cinchonine is dissolved by *concentrated sulphuric acid* to form a colourless solution, which becomes brown and finally black when heated. After the addition of a little *nitric acid* the solution still remains colourless, but, on heating, becomes successively yellowish-brown, brown, and black.

8. A solution of *ammonium vanadate* in *concentrated sulphuric acid* (1 : 100) at first shows no change on the addition of cinchonine, but very gradually assumes a permanent bluish-green coloration.

9. On treating a solution of a cinchonine salt with *chlorine water* no coloration is produced, but on adding ammonia a yellowish-white precipitate is formed. Hence cinchonine does not give a *thalleioquin reaction;* nor does it give an *erythroquin reaction* (Sec. 223, 10). On the other hand, it yields a cinchonine herapathite, analogous to the compound formed by quinine (Sec. 217, 11).

10. On treating a solution of a cinchonine salt, containing at most only a slight trace of free acid, with **potassium ferrocyanide,** a flocculent precipitate of cinchonine hydroferrocyanide, $C_{19}H_{22}N_2O.H_4Fe^{II}(CN)_6.2H_2O$, is produced. On adding an excess of the precipitant, and heating the liquid very gradually, the precipitate dissolves, but separates again, on cooling, in lustrous golden-yellow flakes or long needles, which are frequently united in the shape of a fan. On treating a solution of cinchonine hydrochloride with *potassium ferricyanide*, pointed lemon-yellow crystals of cinchonine hydroferricyanide, $C_{19}H_{22}N_2O.H_3Fe^{III}(CN)_6.2H_2O$, are formed (Ch. Dollfus,[1] Bill,[2] Seligsohn[3]). Both reactions may be used for the microchemical detection of the alkaloid (A. Grutterink[4]).

11. *Tannic acid* gives a white flocculent precipitate with aqueous solutions of cinchonine. The precipitate is soluble in acetic acid and

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[1] *Ann. d. Chem.*, **65**, 212.

[2] *J. Prakt. Chem.*, **75**, 184 (1858).

[3] *Chem. Zentr.*, 1861, 231.

[4] *Zeitsch. anal. Chem.*, **51**, 222 (1912).

also in a little hydrochloric acid, but is re-precipitated on the addition of more hydrochloric acid.

12. Cinchonine is detected by some of the *general precipitation reagents* in more dilute solutions than any other alkaloid. Potassium mercuric iodide still produces an opalescence in a solution diluted to 1 : 600,000 ; iodine in potassium iodide solution gives a precipitate with a solution of 1 : 500,000 ; and phosphomolybdic acid and potassium iodide give a distinct turbidity with a solution of 1 : 200,000. Tannic acid only gives gradually a faint turbidity at 1 : 40,000 ; mercuric chloride at 1 : 10,000 ; and platinum chloride at 1 : 500.

13. With regard to the *microchemical detection*, see the communications of Hesse,[1] Behrens [2] and Grutterink.[3]

Summary and Remarks on Non-Volatile Alkaloids (Group II.)

SEC. 219.

Narcotine may be separated from quinine and cinchonine by repeatedly shaking the acidified solution with chloroform. If the aqueous layer is separated from the chloroform and treated with ammonia and ether containing about 2 per cent. of alcohol, the cinchonine separates, whilst the quinine is obtained in the ethereal solution. On evaporating the chloroform solution the narcotine is obtained, and the quinine by evaporating the ethereal solution. Further tests may readily be applied to the separated alkaloids by means of the reactions described above.

If it is a question not merely of separating quinine and cinchonine from one another, but also of differentiating them from the other alkaloids occurring in cinchona bark—quinidine (optically isomeric with quinine), cinchonidine (optically isomeric with cinchonine), etc.—the test with ammonia solution and ether is not sufficient. Methods for the separation and differentiation of these alkaloids have been given by van der Burg,[4] H. Hager,[5] Hesse,[6] de Vrij,[7] Heilbig,[8] H. Behrens,[9] G. Denigès,[10] and others.

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[1] *Ann. d. Chem.*, **181**, 48, 53.

[2] *Chem. Zentr.*, 1894, II., 105 ; *Zeitsch. anal. Chem.*, **43**, 353 (1904).

[3] *Zeitsch. anal. Chem.*, **51**, 222 (1912).

[4] *Ibid.*, **4**, 273 (1865).

[5] *Ibid.*, **8**, 477 (1869) ; *Pharm. Zentralh.*, **21**, 411 (1880).

[6] *Zeitsch. anal Chem.*, **11**, 328 (1872) ; **28**, 219 ; *Ann. d. Chem.*, **276**, 88, 125.

[7] *Zeitsch. anal. Chem.*, **12**, 320 (1873).

[8] *Ibid.*, **20** 144 (1881) ; **28**, 120 (1889).

[9] *Ibid.*, **43**, 353 (1904).

[10] *Pharm. Ztg.*, **54**, 957 (1909).

Third Group.

Non-volatile alkaloids which are precipitated by potassium hydroxide from solutions of their salts, and are not soluble to any material extent in excess of the precipitant,[1] but are not precipitated from acid solutions, even when fairly concentrated, by alkali hydrogen carbonates.

Strychnine, Brucine, Veratrine, Atropine.

SEC. 220.

1. Strychnine, $C_{21}H_{22}N_2O_2$.

1. *Strychnine* occurs, in association with brucine, in different species of *Strychnos*, and especially in *nux vomica* (the seeds of *Strychnos nux vomica*) and in St. Ignatius beans (the seeds of *Strychnos Ignatii*). It is known either in the form of lustrous white rhombic rods or (when separated by precipitation or rapid evaporation) as a white powder. Strychnine has an alkaline reaction, and an intensely bitter taste, which is perceptible in a dilution of more than 1 : 40,000. It is one of the most deadly poisons ; the most important system is the occurrence of tetanic spasms. One part of strychnine dissolves in 6600 parts of cold and 2500 parts of boiling water, in 1250 parts of ether (containing water), in 180 parts of amyl alcohol, in 165 parts of benzene, in 160 parts of cold and 12 parts of boiling 90 per cent. alcohol, and in 6 parts of chloroform (M. Scholtz[2]). It is nearly insoluble in absolute alcohol, absolute ether, and petroleum spirit. It is lævo-rotatory : $[\alpha]_D = -114{\cdot}7°$ (in alcoholic solution). When heated, it can hardly be melted without decomposition. When cautiously heated, it can be sublimed unchanged in small quantities (Helwig[3]).

2. Strychnine is a mono-acid base. It combines with acids to form *salts*, which as a rule crystallise well, and most of which are soluble in water and dilute alcohol, but are insoluble in ether, chloroform, amyl alcohol, and benzene. All have an intensely bitter taste, and are extremely poisonous. On treating concentrated aqueous solutions with small amounts of acid a portion of the salt separates, but the precipitate re-dissolves on the addition of more acid (Hanriot and Blarez).

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[1] With regard to atropine, *cf.* also Sec. 223, 4.

[2] *Arch. d. Pharm.*, 250, 418 (1912).

[3] *Zeitsch. anal. Chem.*, 3, 46 (1864).

3. *Potassium and sodium hydroxides* and *sodium carbonate* produce white precipitates in solutions of the salts. The precipitate (strychnine) is insoluble in excess of the precipitant, and appears under a magnification of 100 diameters as an aggregate of needle-shaped crystals; in the case of dilute solutions it is only formed after some time, and can then be seen even by the naked eye to consist of needles.

4. *Ammonia* produces a precipitate of the same composition as that formed by potassium hydroxide. This precipitate is soluble in excess of the precipitant. After a short time, however (a considerable time in the case of very dilute solutions), the strychnine separates in acicular crystals, easily recognisable by the naked eye.

5. On treating a *neutral* solution of a strychnine salt with *sodium hydrogen carbonate* strychnine is precipitated after a short time in the form of fine needles. The precipitate is insoluble in excess of the precipitant. If, however, a drop of acid is added (so little that the liquid still remains alkaline), the precipitate which was formed readily dissolves, owing to the action of the liberated carbon dioxide. When an *acid* solution of strychnine is treated with sodium hydrogen carbonate no precipitate is formed. Only after 24 hours, or longer, does the strychnine crystallise from the solution in well-defined prisms, in proportion as the carbon dioxide escapes. If a solution is boiled for some time with excess of sodium hydrogen carbonate, a precipitate is produced, immediately when the solution was concentrated, or only after concentration when it was dilute.

6. Strychnine or a strychnine salt dissolves in concentrated *nitric acid* (sp. gr. 1·4) to form a colourless solution, which becomes yellow on heating. If a small quantity of powdered *potassium chlorate* is added to a solution prepared in the cold, the liquid assumes a fine purple-red coloration. When evaporated with nitric acid strychnine leaves a yellow residue, which becomes orange-yellow on treatment with ammonia, and is changed to reddish-violet by aqueous or alcoholic potassium hydroxide solution (Formánek [1]).

7. If a little strychnine is brought into contact with a few drops of a solution of **ammonium vanadate in concentrated sulphuric acid** (1 : 100) on a clock-glass, the mixture allowed to stand until it becomes of a dark colour, and the clock-glass then slightly inclined, there will be observed at the moment when the vanadium sulphuric acid flows away from the residue a beautiful characteristic blue coloration, which soon changes to a violet and subsequently to a

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[1] *Zeitsch. anal. Chem.*, **36**, 409 (1897).

bright red to reddish-yellow coloration. If the acid is treated with potassium or sodium hydroxide solution as soon as the vermilion-red coloration, appears, a permanent pink to purple-red coloration will be produced, and will become still finer on diluting the liquid with water. The blue coloration is still distinctly visible in the presence of 0·001 mgrm. of strychnine. The reaction is not influenced by the simultaneous presence of other alkaloids, or at all events to a less extent than the following reactions (Mandelin [1]) :—

8. On adding a little strychnine to a few drops of pure **concentrated sulphuric acid** in a porcelain dish a colourless solution is formed. But if a small amount of an **oxidising agent** (potassium chromate, potassium permanganate, potassium ferricyanide, lead peroxide, manganese dioxide), preferably in solid form (for dilution is disadvantageous), there is produced a fine bluish-violet coloration, which changes after some time into wine-red and then into reddish-yellow. In the case of potassium chromate and potassium permanganate the reaction takes place at once ; on inclining the dish bluish-violet streaks are formed by the fragment of the salt introduced, and if this is distributed by shaking, the whole liquid is soon coloured. The appearance of the phenomena is not quite so rapid on the addition of potassium ferricyanide, whilst it is slowest of all with the peroxides. The more rapid the appearance of the coloration, the sooner does the change of colour take place. The reaction is particularly fine and sensitive when produced by means of **potassium dichromate,** as recommended by J. Otto,[2] who pours a dilute solution of the reagent over traces of strychnine on a clock-glass. The strychnine is gradually converted into the sparingly soluble strychnine chromate. If the liquid is decanted, the residue slightly washed with water, the remainder of the liquid absorbed by means of filter paper, and the film of strychnine chromate brought into contact with concentrated sulphuric acid, the blue or bluish-violet streaks are immediately produced. Strychnine chromate may also be precipitated directly from solutions of strychnine salts by means of potassium dichromate (R. Otto). Flückiger recommends the use of a solution of 0·01 grm. of potassium dichromate in 5 c.c. of water, which is mixed with 15 grms. of concentrated sulphuric acid. When the liquid containing the strychnine is poured on to this solution in a test-tube, the bluish-violet zone is formed at the place of contact of the two liquids. The reaction will also

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[1] *Zeitsch. anal. Chem.*, **23,** 240 (1884).

[2] *J. prakt. Chem.*, **38,** 511 (1845).

obviously take place when a trace of strychnine or a strychnine salt is sprinkled on to this reagent.

According to Bailey and Lange,[1] a reaction is obtained with as little as 0·00025 mgrm. of *pure* strychnine when it is moistened with a drop of concentrated sulphuric acid and brought into contact with a particle of a crystal of potassium dichromate.

The method is also very sensitive when the pale green solution of 1 part of potassium permanganate in 2000 parts of concentrated sulphuric acid is used, as was first recommended by Guy. Wenzell[2] states that he has been able unmistakably to detect as little as 0·0005 mgrm. of strychnine by means of this solution. Tartaric acid, citric acid, and thiocyanates, however, behave towards this solution in a similar manner to strychnine (G. Guerin[3]). According to H. Enell,[4] this also applies to many other organic substances, so that it is frequently more advisable to carry out the reaction by means of potassium dichromate. On the other hand, Enell points out that the coloration with chromate is only very indistinct, or is not produced at all, in the presence of nitric acid, or when the strychnine is in the form of a nitric acid salt, and that in such cases, therefore, potassium permanganate should be used. The reaction takes place, however, even when free nitric acid is present, if a large quantity of the reagent is added, the colour then changing from cherry-red (first produced) into violet.

The presence of morphine influences or inhibits this strychnine reaction described above (Reese,[5] Horsley[6]). In order to produce it with certainty in the presence of morphine, the strychnine should first be precipitated as chromate as described above, or the neutral solution should be treated with potassium ferricyanide (Neubauer), and the resulting precipitate washed in the same way, dried and brought into contact with concentrated sulphuric acid. Another method is to separate the strychnine from morphine at the outset by means of chloroform (Rodgers[7]).

With regard to the differentiation of strychnine from brucine by means of this reaction, see Sec. 224.

Finally, it may be mentioned that curarine resembles strychnine in its behaviour towards sulphuric acid and potassium chromate. They may be distinguished, however, by the fact that curarine gives a red coloration with sulphuric acid alone, and that the colorations which it gives with potassium chromate are much more stable. Moreover, curarine may be readily separated from strychnine by means of water or benzene (Dragendorff).

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[1] *Zeitsch. anal. Chem.*, 38, 399 (1899).

[2] *Pharm. Zentralh.*, 2, 234 (1871).

[3] *Zeitsch. anal. Chem.*, 50, 535 (1911).

[4] *Ibid.*, 43, 593 (1904).

[5] *Ibid.*, 1, 399 (1862).

[6] *Ibid.*, 1, 515 (1862).

[7] *Ibid.*, 5, 406 (1866).

9. On adding *ceric oxide* (CeO_2) to a solution of strychnine in concentrated sulphuric acid there is produced a fine blue coloration, which changes relatively slowly into violet, and finally becomes a lasting red (Sonnenschein,[1] Djurberg [2]).

According to Plugge, extremely minute quantities of strychnine (0·0005 mgrm.) may be detected by means of this reaction.

10. On treating a solution of a strychnine salt with strong *chlorine water* a white scum-like precipitate, dissolving in ammonium hydroxide to form a colourless solution, is formed; this is regarded as trichlorostrychnine, $C_{21}H_{19}Cl_3N_2O_2$.

11. According to J. Tafel,[3] strychnine is reduced by *nascent hydrogen* (*e.g.* zinc and hydrochloric acid) to strychnidine and tetrahydrostrychnine. On heating a solution of strychnine in a little hydrochloric acid with excess of zinc dust, filtering the liquid when the evolution of gas has ceased, and treating the filtrate with *ferric chloride*, there is produced a yellowish-red coloration, which is stable on boiling the liquid, and is best obtained when the solution is still slightly acid after the reduction. Ammonia and sodium hydroxide change the yellow coloration of the liquid to red; the colouring matter is not extracted by ether either from the acid or alkaline solution. The test is sensitive to 3 mgrms. of strychinne (W. Lenz [4]). On treating 4 c.c. of a strychnine solution with 4 c.c. of hydrochloric acid (sp. gr. 1·18) and 2 to 3 grms. of granulated zinc, boiling the liquid, allowing the mixture to stand for 4 minutes, and then decanting the supernatant liquid and treating it when cold with one drop of a 0·1 per cent. solution of sodium nitrite to 2 c.c., a red coloration is immediately produced in the presence of 0·003 to 0·004 mgrm. of strychnine. If, instead of the nitrite, 1 c.c. of sulphuric acid and a drop of 0·1 per cent. sodium nitrate solution are used, the red coloration produced is much more intense, but the reaction applied in this form is somewhat less sensitive (P. Malaquin,[5] G. Denigès [6]).

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[1] *Zeitsch. anal. Chem.*, **9**, 494 (1870).
[2] *Ibid.*, **11**, 440 (1872).
[3] *Ann. d. Chem.*, **301**, 285 (1898).
[4] *Pharm. Zeit.*, **43**, 786 (1898).
[5] *Zeitsch. anal. Chem.*, **49**, 656 (1910).
[6] *Ibid.*, **51**, 158 (1912).

12. On treating a solution of a strychnine salt with *potassium thiocyanate* a crystalline white precipitate is produced, immediately in concentrated, and after some time in more dilute, solutions; under the microscope this precipitate is seen to consist of flat needles with blunt or pointed ends; they are only slightly soluble in excess of the precipitant.

13. Mercuric chloride produces in solutions of strychnine salts a white precipitate, which after some time changes into stellar groups of needles, plainly visible with the aid of a lens. On heating the liquid they dissolve; and on cooling the solution the compound is obtained in large crystals.

14. Tannic acid produces a compact white precipitate, insoluble in hydrochloric acid, in solutions of strychnine salts containing as little as 1 : 3000.

15. Of the other *general precipitation reagents*, potassium mercuric iodide produces a compact white precipitate, and gives a turbidity with solutions containing 1 : 150,000; iodine in potassium iodide solution produces a precipitate of reddish-brown colour in a solution containing 1 : 15,000; phosphomolybdic acid produces a yellowish-white precipitate with solutions of 1 : 14,000; and gold chloride gives a dirty yellow precipitate with solutions of 1 : 10,000, this precipitate being soluble in alcohol, and crystallising therefrom in orange-yellow crystals. Platinum chloride produces, even in solutions containing 1 : 1000, a yellowish-white precipitate, which dissolves with difficulty in boiling alcohol and separates therefrom in lustrous flakes (Dragendorff). In a solution slightly acidified with nitric acid, potassium bismuth iodide is stated to give a precipitate in the presence of 1 part of the alkaloid in 40,000, and phosphotungstic acid with 1 : 100,000.

16. With regard to the *microchemical detection* see the communications of A. Grutterink[1] and R. Wasicky.[2]

SEC. 221.

2. Brucine, $C_{23}H_{26}N_2O_4$.

1. *Brucine*, which occurs in association with strychnine in different species of *Strychnos* (*cf.* p. 887), is known in the crystalline condition, $C_{23}H_{26}N_2O_4{\cdot}4H_2O$, either in the form of transparent rhombic rods or stellar groups of needles, or as a white powder com-

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[1] *Zeitsch. anal. Chem.*, **51**, 187 (1912).

[2] *Zeitsch. allgem. österr. Apoth. Vereins*, **52**, 35, 41, 53, and 67 (1914).

posed of small crystalline flakes. It has a bitter taste and a toxic action, which, however, is less pronounced than that of strychnine. Crystallised brucine dissolves in 320 parts of cold and in 150 parts of boiling water, whilst the anhydrous alkaloid dissolves in 850 and 500 parts respectively. It is also soluble in 1140 parts of petroleum spirit, and in 1325 parts of ether containing water, but is very sparingly soluble in absolute ether; it dissolves in 2 parts of 80 per cent. alcohol, and is also readily soluble in absolute alcohol, in amyl alcohol (especially on heating), and in chloroform. It is lævo-rotatory: $[\alpha]_D$ in absolute alcohol solution $= -80{\cdot}1°$, in chloroform solution $= -120°$. It melts at 100° in its water of crystallisation, whilst the anhydrous brucine melts at 178°.

2. Brucine is a mono-acid base, and combines with acids to form *salts*, which are readily soluble in water and have a very bitter taste, and most of which are crystallisable.

3. *Potassium hydroxide*, *sodium hydroxide*, and *sodium carbonate* precipitate brucine from solutions of its salts as a white precipitate insoluble in excess of the precipitant. When examined under the microscope immediately after the precipitation it appears to consist of very small granules. On continuing the observation, however, these will be seen to coalesce suddenly (with the fixation of water) into needles, which again invariably group themselves concentrically. This alteration in the precipitate may even be observed with the naked eye.

4. *Ammonia* precipitates brucine from solutions of its salts as a white precipitate. At first this appears to be composed of minute drops of oil, but these gradually combine with water and change into minute needles. The precipitate is readily soluble, immediately after the precipitation, in an excess of ammonia solution. After a very short time, however (somewhat longer in the case of dilute solutions), the brucine combined with water of crystallisation crystallises from the solution in small needles grouped concentrically, and is then no longer dissolved by the addition of more ammonia solution.

5. *Sodium hydrogen carbonate*, added to a neutral solution of brucine, produces in a short time a precipitate of brucine (containing water of crystallisation) in the form of lustrous silken needles grouped concentrically. The precipitate is insoluble in excess of the precipitant, but dissolves through the action of free carbon dioxide (*cf.* Sec. 220, 5). Acid solutions of brucine salts do not give a precipitate Only after a long time, as the carbon dioxide escapes,

does the above-mentioned compound separate in relatively large crystals.

6. On bringing brucine or one of its compounds into contact with **concentrated nitric acid** (sp. gr. 1·3 to 1·4), a solution is obtained which is momentarily an intense bright red, and then yellowish-red, and changes to yellow on heating. If the liquid, whether concentrated or diluted with water, is treated, drop by drop, after being heated to this point, with **stannous chloride solution** diluted with a little water, the intense yellow coloration changes to an extremely intense violet. A violet precipitate is also formed in concentrated solutions. This reaction is also produced by colourless ammonium sulphide solution. The smaller the quantity of nitric acid used for the solution of the brucine, the finer is the coloration. If sodium hydrogen sulphide solution is used instead of the reducing agents mentioned, the violet coloration first produced changes subsequently to green (St. Cotton [1]). The stannous chloride reaction is particularly fine when about 0·5 c.c. of a solution of brucine in 60 per cent. chloral hydrate solution is mixed with a very little dilute nitric acid, and the mixture poured on to three times its volume of concentrated sulphuric acid. A yellowish-red to deep red coloration is immediately produced. When the upper layer has become yellow after a short time, a little dilute stannous chloride is introduced by means of a pipette. (This solution is prepared by dissolving 1 part of stannous chloride in 9 parts of hydrochloric acid of sp. gr. 1·12.) A fine violet zone then appears between the two upper layers (R. Mauch [2]).

7. On mixing a little brucine with a few drops of *concentrated sulphuric acid* a colourless solution is obtained. If, however, the sulphuric acid contained a trace of *nitric acid*, or if **Erdmann's reagent** (Sec. 216, 6) is used, a transitory pink to red coloration and subsequently a yellow coloration is obtained. The reaction is very sensitive.

8. When brucine is brought into contact with a solution of *ammonium vanadate* in *concentrated sulphuric acid* (1 : 200), the solution becomes transitorily red and then reddish-orange, and is soon decolorised (Mandelin [3]).

9. On treating the solution of a brucine salt with *potassium dichromate*, it remains clear at first, but after some time yellowish-red crystals separate, which dissolve in concentrated sulphuric acid

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[1] *Zeitsch. anal. Chem.*, **9**, 111 (1870).

[2] *Über physikalisch-chemische Eigenschaften des Chloralhydrats*, Dissert. Strassburg, 1898, p. 34.

[3] *Zeitsch. anal. Chem.*, **23**, 236 (1884).

to form a brownish-red solution. On drawing a small crystal of potassium dichromate through a colourless solution of brucine in sulphuric acid (free from nitric acid) red streaks are formed, and the whole liquid then becomes red, changing to olive-green, to brown, and finally to green (Gadamer). On dissolving brucine in dilute sulphuric acid (1 : 10), and introducing into the solution a glass rod previously dipped into very dilute potassium dichromate solution, a raspberry-red coloration is first produced, but changes into orange and brownish-yellow (Dragendorff [1]).

10. When a solution of brucine in acetic acid is diluted with water and then treated with *lead peroxide*, the liquid becomes pink (Ihl). When treated with *manganese dioxide* and dilute sulphuric acid in the cold, brucine gives a yellowish-red to blood-red coloration in a few hours, and *picric acid* then added to the filtrate produces an amorphous yellow precipitate (H. Hager [2]).

11. On mixing a solution of a brucine salt with a solution of **mercurous nitrate,** as free from acid as possible, a colourless liquid is obtained. On now heating the mixture on a moderately hot water bath, a fine carmine coloration gradually develops from the margin and increases in intensity; it is very stable. Strychnine does not produce a red coloration. In this way 1 part of brucine may be detected in the presence of 10 to 20 parts of strychnine (Flückiger [3]). As was pointed out by C. Reichard,[4] the reaction does not take place with the free alkaloid, but only with brucine salts. In the reaction between free brucine and the mercurous salt, the latter is reduced to metallic mercury, which gradually separates as a whitish-grey mass, which finally becomes almost black.

12. When a solution of a brucine salt is carefully treated with **chlorine water** it becomes bright red, the colour changing on the addition of ammonia solution to pale yellowish-brown. If solid brucine is treated with a little chlorine water it dissolves, forming a pale-red solution, which, when evaporated on the water bath, leaves a blood-red residue (Beckurts). (Essential distinction from strychnine.)

13. On treating solutions of brucine salts with *potassium thiocyanate* a granular crystalline precipitate is formed, especially when the sides of the vessel are rubbed, immediately in concentrated, and after some time in dilute, solutions. Under the microscope the

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[1] *Zeitsch. anal. Chem.*, **18**, 107 (1879)

[2] *Ibid.*, **11**, 201 (1872).

[3] *Ibid.*, **15**, 342 (1876).

[4] *Ibid.*, **49**, 700 (1910).

precipitate shows the form of polyhedric crystalline granules grouped in various ways with regard to each other.

14. *Mercuric chloride* produces a white granular precipitate, which under the microscope is seen to consist of minute globular crystalline granules.

15. *Tannic acid* produces a compact dirty-white precipitate in solutions of brucine salts containing as little as 1 : 2000; the precipitate is soluble in acetic acid, but insoluble in hydrochloric acid.

16. Of the remaining *general precipitation reagents*, iodine in potassium iodide solution reacts with solutions diluted to 1 : 50,000; potassium mercuric iodide with solutions containing 1 : 30,000; gold chloride with 1 : 20,000; potassium bismuth iodide and also molybdic acid with 1 : 50,000; and platinum chloride with 1 : 1000 (Dragendorff). The ochre-yellow phosphomolybdic acid precipitate gives the reaction described in 6.

SEC. 222.

3. Veratrine.

1. *Veratrine* is a mixture of two isomeric alkaloids, not easily separated, which are contained in sabadilla seeds (*Sabadilla officinalis*), viz. crystallisable *cevadine* and amorphous *veratridine*, each of which has the formula $C_{32}H_{49}NO_9$. For toxicological investigations this mixture is to be regarded as an individual substance.[1] It is a bulky white odourless powder, with a pungent burning but not bitter taste, and is extremely toxic. Its dust provokes violent sneezing. It is only very slightly soluble in water: to a greater extent in the freshly precipitated than in the dry condition. The solution has a burning taste, and is faintly alkaline in its reaction. The cold saturated solution becomes turbid when heated, but becomes clear again on cooling, provided that the heating was not continued too long. Veratrine dissolves in 2 parts of chloroform, in 3 parts of alcohol, and in 10 parts of ether, somewhat readily in amyl alcohol and in benzene, and to a still smaller extent in petroleum spirit. It melts like a wax at 150°–155°, and, on cooling, solidifies to a yellow transparent mass; when carefully heated it can be sublimed unchanged.

2. Acids neutralise veratrine completely. Some of the *salts* crystallise with difficulty, but most of them resemble gums when dry. Some of them are soluble in water and have a pungent burning

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[1] The statements in the text refer to the "officinal veratrine." With regard to the separation of the mixed alkaloids, see E. Schmidt and R. Köppen (*Ann. d. Chem.*, **185**, 224) and Bosetti (*Zeitsch. anal. Chem.*, **25**, 249 (1886)).

taste. Veratrine is extracted from acid solutions by benzene, but not by petroleum spirit (Masing).

3. *Potassium and sodium hydroxides*, *ammonia* and *alkali carbonates* produce in solutions of veratrine salts a flocculent white precipitate, which, when examined under the microscope immediately after precipitation, is seen to be non-crystalline. After some minutes, however, it changes its condition, and instead of the coagulated mass, of which at first it appeared to consist, crystalline groups composed of short rods are visible. The precipitate is not insoluble in excess of potassium or sodium hydroxide solution or of potassium carbonate solution. It is slightly soluble in ammonia solution in the cold, but, on heating, the dissolved portion partially separates again.

4. The salts of veratrine behave like those of strychnine and brucine towards *sodium* or *potassium hydrogen carbonates*. On boiling the solution, however, veratrine readily separates from dilute solutions.

5. When veratrine is dissolved in **concentrated hydrochloric acid** it yields a colourless solution, which, when boiled for some time, gradually becomes reddish and finally intense red, and the colour of which does not disappear on standing. The reaction is very sensitive (Trapp [1]).

6. On bringing veratrine into contact with **concentrated nitric acid** it agglomerates into resinous lumps, which slowly dissolve. If the veratrine was pure the solution is colourless. On evaporating the solution to dryness on the water bath, and heating the residue with **alcoholic potassium hydroxide solution** (1 : 10), it assumes a blood-red or, in the case of smaller quantities, a raspberry-red coloration; at the same time, on evaporating the alcohol, an odour of coniine becomes perceptible, and is reproduced on repeating the addition of alcoholic potassium hydroxide solution. This odour of coniine can be recognised in the presence of 0·25 mgrm., whilst the raspberry-red coloration is not produced until the amount of the alkaloid reaches 1·3 mgrm. (J. Konkadow [2]).

7. When veratrine is introduced into *concentrated sulphuric acid* it agglomerates in like manner into a resin-like mass. The lumps readily dissolve, however, to form a solution which at first is yellow with a greenish-yellow fluorescence, but the yellow colour of which becomes continually darker, and then changes through reddish-yellow into an intense blood-red, and finally to purple-red; the colour persists for

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[1] *Zeitsch. anal. Chem.*, **2**, 215 (1863).

[2] *Chem. Zeit.*, **23**, 4 (1899).

two or three hours and then gradually fades. On heating the liquid the red coloration is produced immediately. The addition of about an equal volume of bromine water also causes the yellow colour of the fresh sulphuric acid solution to change at once into purple-red. Cubebine also gives a similar reaction (Schär). Erdmann's reagent (Sec. 216, 6) and Fröhde's reagent (Sec. 213, 11) act in the same way as concentrated sulphuric acid, but somewhat more rapidly.

8. A solution of *ammonium vanadate* in *concentrated sulphuric acid* (1 : 100) is at first changed to brownish-red and subsequently to dark reddish-violet by veratrine (Kundrat).

9. If a little powdered **sugar** is sprinkled over a thin layer of the yellow solution of veratrine in **concentrated sulphuric acid** there is soon produced (owing to dehydration) a dark green coloration, which gradually becomes intense blue and then slowly fades (Weppen[1]). The formation of the green coloration is accelerated by breathing on the mixture. The blue coloration is particularly fine when it is obtained by adding a small drop of **bromine water** to the mixture after it has become green. If the quantity of veratrine is not too small it may be ground up with the sugar, and the mixture then stirred with a few drops of concentrated sulphuric acid. The success of the reaction depends upon there being a definite proportion between the amounts of veratrine and sugar; according to Beckurts this should be 1 : 6. R. Otto was unable to obtain the reaction with a mixture in the proportions of 1 : 2 and 1 : 4 originally prescribed by Weppen; it could be obtained with a mixture of 1 : 8, but the colorations were not nearly so fine as with the mixture of 1 : 6.

10. On treating veratrine with a solution of five drops of furfural in 10 c.c. of concentrated sulphuric acid, the liquid becomes first yellow to olive-green with blue margins, and then, after a few minutes, the colour changes to sap-green and finally to a fine blue (N. Wender[2]). The reaction is not so sensitive as the preceding one.

11. On treating a solution of a veratrine salt with not too small a quantity of *chlorine water*, it becomes intensely yellow, and the coloration is not materially changed on adding ammonia.

12. The most sensitive of the *general precipitation reagents* for alkaloids in the case of veratrine are iodine in potassium iodide solution, potassium mercuric iodide, phosphomolybdic acid, and tannin; they produce precipitates even in solutions diluted to 1 : 5,000.[3]

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[1] *Zeitsch. anal. Chem.*, **13**, 454 (1874).

[2] *Ibid.*, **42**, 328 (1903).

[3] With regard to the further reactions of veratrine, *cf.* C. Reichard, *Pharm. Zentralh.*, **46**, 644 (1905).

SEC. 223.

4. Atropine, $C_{17}H_{23}NO_3$.

The i-Tropine ester of (d+l) tropic acid.

$C_6H_5.CH(CH_2.OH).COO.C_7H_{11}N(CH_3)$.

1. *Atropine*, which occurs in all parts of the deadly nightshade (*Atropa belladonna*) and the thorn apple (*Datura stramonium*), in association with the isomeric hyoscyamine (Ladenburg, E. Schmidt),[1] is known in the form of colourless lustrous rods and needles. It is odourless, and has a nauseous and persistent bitter taste. Atropine is soluble in about 300 parts of water (Planta) and in 1211 parts of petroleum spirit at about 20°, in 45 parts of ether, 26 parts of ethyl acetate, 25 parts of benzene, and 1·5 parts of chloroform (M. Scholtz). It is readily soluble in alcohol and amyl alcohol. It is optically inactive. Its aqueous solution has an alkaline reaction; on boiling it some of the atropine volatilises with the steam. Atropine is extracted from the solution by treatment with animal charcoal. The alkaloid melts at 115° to 115·5°. When carefully heated above that temperature the greater portion of the atropine volatilises unaltered, and sublimes at first in oily drops, which, when in contact with a drop of water, gradually yield crystalline needles, and, on contact with hydrochloric acid, form fine octahedra after some time (Helwig[2]).

2. Atropine combines with acids to form *salts*, most of which are non-crystalline or only crystallise with difficulty. The salts are readily soluble in water and alcohol, but are practically insoluble in ether, benzene, and amyl alcohol. Aqueous solutions of atropine salts darken when heated for some time.

3. *Atropine* and *atropine salts* have a poisonous narcotic action. They are mydriatic, *i.e.* enlarge the pupil for a considerable time when introduced into the eye. The same effect, however, is also produced by hyoscyamine. In the case of the latter alkaloid the action takes place at a somewhat later period, but is more lasting than in the case of atropine. Cocaine also enlarges the pupil, but only when a somewhat concentrated solution is used. According to Donders and Ruyter, one drop of a solution of atropine (1 : 130,000) will still produce mydriasis.

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[1] E. Schmidt and H. Henschke (*Chem. Zentr.*, 1888, 549) also found atropine in association with hyoscyamine and scopolamine in the root of *Scopolia japonica*. With regard to other alkaloids accompanying atropine and hyoscyamine in belladonna and their properties, see O. Hesse (*Ann. d. Chem.*, 261, 87; 271, 100).

[2] *Zeitsch. anal. Chem.*, 3, 43 (1864).

4. *Potassium and sodium hydroxides* and *alkali carbonates* precipitate part of the atropine from concentrated aqueous solutions of atropine salts. The precipitate, which is pulverulent at first, does not dissolve more readily in excess of the precipitant than in water. On standing for a considerable time it becomes crystalline. *Ammonia* also precipitates the alkaloid; the precipitate is soluble in excess of the precipitant. On treatment with fixed alkalis, and also with baryta water, atropine is decomposed, slowly in the cold and more rapidly on heating, with the formation of tropic acid and subsequently of atropic acid (α-phenylacrylic acid) and also of tropine.

5. *Ammonium carbonate* and *alkali hydrogen carbonates* do not precipitate atropine from solutions of its salts.

6. If atropine or an atropine salt is treated with a little fuming **nitric acid,** and the mixture dried on the water bath, a colourless residue is obtained. On adding to this, when cold, a drop of a solution of **potassium hydroxide** in absolute alcohol, a violet coloration, soon changing to red. is produced (Vitali [1]). The test is capable of detecting 0·001 mgrm. Hyoscyamine and scopolamine give the same, and strychnine and veratrine an analogous reaction. With regard to the difference in the behaviour of strychnine and atropine, see D. Vitali.[2]

7. On heating atropine with *concentrated sulphuric acid* until a brown coloration appears, and then adding twice the volume of water, the mixture froths up and emits a sweet odour, recalling that of sloe blossoms (Gulielmo [3]). On then adding to the hot mixture a granule of *potassium dichromate,* the resulting odour will recall that of meadowsweet (*Spiræa ulmaria*); whilst on continuing the heating it will resemble that of bitter almonds (Pfeiffer). The odour of flowers, which is characteristic of atropine, may also be produced by placing a little of the alkaloid upon crystals of chromic acid, and heating the mixture until, owing to incipient reduction, the chromic acid becomes green (Brunner [4]).

8. If atropine is brought into contact with *concentrated sulphuric acid* on a white porcelain surface, and a few crystals of *potassium nitrate* stirred into the mixture, a deep yellow to orange coloration is produced. On then adding a few drops of an alcoholic solution

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[1] *Zeitsch. anal. Chem.*, **20,** 563 (1881).

[2] *Ibid.*, **38,** 134 (1899).

[3] *Ibid.*, **2,** 404 (1863).

[4] *Ber.*, **6,** 98 (1873); *Zeitsch. anal. Chem.*, **12,** 345.

of potassium hydroxide the mixture assumes a fine reddish-violet coloration, which soon changes to pale pink (Arnold).

9. *Auric chloride* precipitates from aqueous solutions of atropine salts the aurochloride, $C_{17}H_{23}NO_3.HAuCl_4$, in the form of a yellow precipitate, which is sometimes oily at first, but gradually becomes crystalline. When recrystallised from hot water containing hydrochloric acid, this compound is obtained in small lustreless flakes, which melt at 135° to 137° (Landenburg [1]).

10. An aqueous solution of mercuric chloride, added to an alcoholic solution of an atropine salt, immediately produces a yellowish precipitate, changing to orange-red when gently heated (Gerrard).

11. *Tannic acid* produces in absolutely neutral aqueous solutions of atropine salts a caseous white precipitate, which is soluble both in hydrochloric acid and in ammonia solution.

12. *Picric acid* produces a crystalline precipitate in acid solutions of atropine which are not more dilute than 1 : 500. If, however, the so-called *atropinum sulphuricum naturale*, which is a mixture of atropine and hyoscyamine sulphates, is used for the reaction, an amorphous turbidity, changing to oily drops, is produced.

13. Of the other *general precipitation reagents*, the following produce precipitates in slightly acid (sulphuric acid) solutions: Potassium mercuric iodide in solutions containing 1 : 150,000; iodine in potassium iodide solution with 1 : 65,000; and phosphomolybdic acid with 1 : 16,000.[2]

Summary and Remarks on Non-Volatile Alkaloids (Group III.).

SEC. 224.

Strychnine may be separated from brucine, veratrine, and atropine by means of cold *absolute* alcohol, in which it is soluble, whilst the other two are insoluble. The separation of strychnine and brucine, which may be required in cases of *nux vomica* poisoning, may be effected by means of potassium dichromate. For this purpose, the alkaloids are obtained in a solution as concentrated as possible in dilute acetic acid, and potassium dichromate added. Under these conditions nearly the whole of the strychnine separates as chromate, whilst the brucine remains in solution; after standing for a considerable time, however, the brucine may also separate as chromate (R. Otto). The two alkaloids may also be readily differentiated and separated by means of chlorine water; for when treated in the dry condition with that reagent the brucine dissolves to form a red solution (Sec. 221, 12), whilst the strychnine is left undissolved (Sec. 220, 10) (Beckurts[1]). According to Beckurts[2] the most accurate method of separating the two alkaloids is to treat the mixture, which must previously be purified as completely as possible, with water containing hydrochloric acid, so as to obtain an approximately 1 per cent. solution, and to add 0·5 per cent. potassium ferrocyanide solution to this, with constant stirring, until a drop of the mixture, filtered through a micro-filter, produces a blue coloration on moist filter paper impregnated with ferric chloride solution. Only the strychnine is thus precipitated as hydroferrocyanic acid salt. Strychnine is best identified by the reaction with sulphuric acid and the oxidising agents mentioned in Sec. 220, 8,[3] and by its microchemical behaviour. Brucine and veratrine may be separated from atropine by rendering the solution alkaline and shaking it with petroleum spirit (Dragendorff), this solvent extracts the brucine and veratrine, but not the atropine. On shaking the aqueous layer, separated from the petroleum spirit, with ether, the atropine is then obtained in ethereal solution. There is no good method of separating brucine from veratrine, but they may be readily identified in the presence of each other. For this purpose the reaction described in Sec. 221, 6, is the most suitable for brucine. To distinguish veratrine from brucine, as also from all the other alkaloids dealt with here, it is sufficient to observe its behaviour on melting (Sec. 221, 1), a characteristic which it shares with none of the others. In order to detect it in the presence of brucine, the reaction with hydrochloric acid or with concentrated sulphuric acid (Sec. 221, 5 and 7) should be used.

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[1] *Ann. d. Chem.*, **206**, 274.

[2] With regard to the reactions of atropine, *cf.* also C. Reichard, *Chem. Zeit.*, **28**, 1048 (1904), and K. Eder, *Zeitsch. anal Chem.*, **58**, 233.

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[1] *Zeitsch. anal. Chem.*, **28**, 102 (1889).

[2] *Arch. d. Pharm.*, **228**, 315 (1890); *Zeitsch. anal. Chem.*, **29**, 730.

[3] The only substances besides *curarine* (Sec. 220, 8) which show a somewhat similar behaviour in this respect are *aniline* (Beissenhirz, *Ann. d. Chem.*, **87**, 376 (1853)) and all *acyl-anilines* or *acyl-tetrahydroquinolines* (J. Tafel, *Ber.*, **25**, 412 (1892)), the *p*-position of which is not occupied. A. Guy, however, calls attention to the fact that aniline, when treated with sulphuric acid and oxidising agents, becomes first pale green, then gradually darkens, and only then assumes a fine blue colour, which persists for a long time and finally changes to black. Brucine interferes to a considerable extent with the colour reaction of strychnine with concentrated sulphuric acid and potassium dichromate. The reaction is still perceptible, however, with 1 mgrm. of strychnine in the presence of 20 mgrms. of brucine, but is indistinct with 1 mgrm. to 40 mgrms. (Beckurts).

C. PROPERTIES AND REACTIONS OF CERTAIN NON-NITROGENOUS SUBSTANCES ALLIED TO THE ALKALOIDS.

Although they do not belong to the class of alkaloids, and differ fundamentally from them in being free from nitrogen, the substances salicine, digitaline, and picrotoxine may be dealt with as a supplement to the alkaloids which have been described.

SEC. 225.

1. Salicine, $C_{13}H_{18}O_7$.

Saligenine glucoside, $C_6H_4(CH_2.OH).O.C_6H_{11}O_5$.

1. *Salicine* occurs in the bark and leaves of most willows (*Salix*) and of certain species of poplars (*Populus*), also in poplar buds and the buds of meadowsweet (*Spiræa ulmaria*). It is known either in the form of lustrous white needles and spangles, or, if these are very fine and small, as a lustrous powder. It has a bitter taste. It dissolves with some difficulty in 28 parts of cold water or in 30 parts of cold alcohol, but is readily soluble in the boiling solvents. It is insoluble in ether, but is soluble in potassium hydroxide solution and in glacial acetic acid. It is lævo-rotatory, with $[\alpha] = -66°$. It melts at 201°; on continuing the heating it solidifies again, and is decomposed at 230°–240°, with the liberation of dextrose and condensation of the residue of saligenin to *saliretin*, $HO.C_6H_4.CH_2.O.C_6H_4.CH_2.OH$ (Schiff[1]).

2. Salicine does not neutralise acids, and does not combine with them.

3. When salicine is brought into contact with **concentrated sulphuric acid** it assumes a blood-red coloration and agglomerates into resin-like masses. The sulphuric acid itself remains colourless at first. Solution takes place only slowly, the acid becoming increasingly red as it proceeds, whilst water will then produce in it a red precipitate which is soluble in water but insoluble in dilute sulphuric acid (Braconnet,[2] Mulder[3]).

4. On treating an aqueous solution of salicine with **dilute sulphuric acid** or with **hydrochloric acid,** and gently heating the mixture, the *salicine* is decomposed into dextrose and saligenin (*o*-hydoxybenzyl alcohol, $HO.C_6H_4.CH_2.OH$) (Piria[4]). If, however, the liquid is *boiled* for a short time, it suddenly becomes turbid,

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[1] *Ber.*. **14**, 304 (1881).

[2] *Ann. chim. phys.*, (2) **44**, 296.

[3] *J. prakt. Chem.*, **18**, 356.

[4] *Ann. chim. phys.*, (3) **14**, 257.

while the saligenin undergoes further decomposition into saliretin (*cf.* 1, *supra*) (Piria [1]), which separates as a flocculent white agglomerating precipitate. On adding one or two drops of *potassium dichromate solution* to the liquid containing the precipitate and boiling the mixture, the saliretin becomes bright pink, while at the same time the characteristic pleasant aromatic odour of salicylic aldehyde is emitted. If the boiling with dilute sulphuric acid and potassium dichromate is carried out in a small distillation flask connected with a receiver containing a little water, the salicylic aldehyde may easily be detected in the distillate by adding a drop of neutral ferric chloride solution, which will produce an intense violet coloration (Parrot). Salicine is not decomposed when heated with alkali solution.

5. On moistening a little salicine with a few drops of a solution of pure *zinc chloride* in dilute hydrochloric acid (0·1 grm. of fused zinc chloride, 3 c.c. of concentrated hydrochloric acid, and 3 c.c. of water), and drying the mixture on the water bath, an intense violet-red residue is obtained (A. Jorissen).

6. There is scarcely any reagent which precipitates salicine without causing its simultaneous decomposition. *Lead acetate*, however, precipitates lead salicine, $C_{13}H_{14}O_7Pb_2$, as an amorphous powder, soluble in acetic acid and alkali solutions, from concentrated hot aqueous solutions (Piria [2]) and *sodium ethyl alcoholate* precipitates *sodium salicine*, $C_{13}H_{17}O_7Na$, as a white, very friable mass from alcoholic solutions of salicine (Perkin [3]).

7. *Ferric chloride* produces only a very slight brownish coloration in solutions of salicine, but on boiling the liquid it is decolorised, while an ochre-yellow precipitate is formed.

8. When salicine is added to a solution of 3 grms. of *silver nitrate* in 30 grms. of ammonia solution of sp. gr. 0·923, to which has been added a solution of 3 grms. of sodium hydroxide in 30 c.c. of water, and the mixture is heated, a silver mirror is formed, owing to the reduction of the silver salt. Other glucosides, mannitol, cane sugar, and also dextrose give the same reaction (E. Salkowski).

SEC. 226.

2. Digitaline.

1. The preparations sold under the name of *digitaline* in commerce vary very greatly in their composition. They consist of

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[1] *Ann. chim. phys.*, (2) **69**, 281.
[2] *Ibid.*, (2) **69**, 281.
[3] *Zeitsch. f. Chem.*, 1869, 126.

mixtures of the active constituents of those parts of the red foxglove (*Digitalis purpurea*) which grow above the soil. These have the characteristics of glucosides, and among them the following have been identified with certainty as definite individuals[1]: *Digitoxine*, $C_{34}H_{54}O_{11}$; crystallisable *digitonine* $(C_{27}H_{46}O_{14}.5H_2O)_2$; true *digitaline* in the narrower sense of the word, $C_{35}H_{56}O_{14}$ or $C_{36}H_{58}O_{14}$, and the still less known *digitaleine*, $C_{28}H_{48}O_{10}$. Digitoxine, digitaline, and digitaleine are cardiac poisons, the first and the last in particular having a very pronounced action; digitonine is also toxic, but is not a cardiac posion. When boiled with alcoholic hydrochloric acid, these glucosides undergo hydrolytic dissociation. Digitoxine yields digitoxigenine ($C_{22}H_{32}O_4$) and 2 molecules of digitoxose ($C_6H_{12}O_4$); from digitonine are formed digitogenine ($C_{30}H_{48}O_6$), 2 molecules of dextrose, and 2 molecules of galactose; whilst true digitaline yields digitaligenine ($C_{22}H_{30}O_3$), digitalose ($C_7H_{14}O_5$), and dextrose.

2. Of these pure glucosides only digitoxine, digitonine, and digitaline can be obtained commercially at the present time. True digitaline (*digitalinum verum*) is not a commercial product. With regard to the other preparations sold under the name of digitaline the following remarks may be made: *Digitalinum purum amorphum* (*digitalinum gallicum*, Homolle's amorphous digitaline) of the French and Belgian Pharmacopœias is prepared from digitalis leaves, and consists, in the main, of digitoxine. *Digitalinum germanicum* is obtained from the seeds, and contains true digitaline and digitaleine, with about 50 per cent. of digitonine. Lastly, mention must be made of true digitonine, which is sold under the name of "*digitalin cryst.*" In view of the fact that there are all these various preparations, it can be understood that the communications upon the behaviour and reactions of "digitaline" are not free from contradictions, since some of them do not refer to preparations of the same kind. In the following outline we have endeavoured to give only statements referring to materials the nature of which was definitely established. It may also be noted that in the forensic detection of digitalis poisoning, predominant attention must be given to digitoxine, since the other glucosides can hardly be detected in experimental mixtures with cadaveric remains, and *a fortiori* disappear in the organism.

3. *Digitoxine* forms tabular white crystals containing water of

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[1] O. Schmiedeberg, *Arch. experm. Pathol.*, **3**, 16 (1875); H. Kiliani, *Arch. d. Pharm.*, **230**, 250; **231**, 460; **233**, 299, 311, 698; **234**, 273, 481; **237**, 446; **243**, 5; **252**, 13; **254**, 255; C. C. Keller, *Zeitsch. anal. Chem.*, **39**, 257; F. Kraft, *Arch. d. Pharm.*, **250**, 118 (1912).

crystallisation. In this condition it melts at 145°–150°, and when anhydrous, at 245°–246°. It dissolves in about 2000 parts of water; it is almost insoluble in ether, but dissolves in 15 parts of hot 70 per cent. alcohol, and is readily soluble in chloroform and in a mixture of glycerin, water, and alcohol. *Digitonine* forms colourless needles or wart-like structures, which soften and turn yellow above 235°, without showing any sharp melting-point. It is only sparingly soluble in water, ether, and chloroform, but dissolves in 57 parts of absolute alcohol, with more difficulty in dilute alcohol, and more readily in a mixture of alcohol and chloroform. It can only be extracted with difficulty by chloroform, but more easily by amyl alcohol. *True digitaline* forms white needles, partly united into wart-like masses; it sinters at 210° and melts at 217°, meanwhile turning yellow. In the pure condition it dissolves with difficulty in water (in about 1000 parts) and in ether, but is more soluble in alcohol and in chloroform. Amyl alcohol is the best solvent for its extraction. *Digitaleine* is an amorphous white powder with a bitter taste; it dissolves in 600 parts of water, and is soluble in alcohol (the solution decomposes after some time), readily soluble in chloroform, but insoluble in petroleum spirit. *Digitalin Homolle* is a yellow powder, soluble in alcohol and chloroform and in 2000 parts of water, but dissolving with difficulty in ether. *German digitaline* is a yellowish-white powder, which dissolves in cold water to form a neutral, turbid, bitter solution, which froths strongly when shaken. It is completely soluble in alcohol and amyl alcohol, partially soluble in ether, benzene, and chloroform, and insoluble in petroleum spirit.

4. *Behaviour towards concentrated hydrochloric acid.* When heated with concentrated hydrochloric acid *digitoxine* gives a green to brownish-green coloration. On heating *digitonine* with hydrochloric acid of sp. gr. 1·19 for five minutes on a boiling water bath the solution becomes yellow, then darkens and changes to red, to deep garnet-red, and finally shows an indication of blue. On diluting the liquid, after cooling, with four times its volume of water a blue solution with red fluorescence is obtained; the colour soon fades and the liquid becomes turbid (C. C. Keller [1]). *True digitaline* dissolves, forming a golden yellow solution, which becomes brown on heating. *Digitaleine* gives a pale yellow solution.

5. *Behaviour towards concentrated sulphuric acid. Digitonine* dissolves in concentrated sulphuric acid to form a bright red solution, which gradually darkens, and finally becomes reddish-violet. The

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[1] *Zeitsch. anal. Chem.*, **39**, 529 (1900).

coloration is obtained with 0·02 mgrm. (Dragendorff[1]). *True digitaline* dissolves in sulphuric acid, forming a greenish-yellow solution, the colour of which changes successively to golden-yellow, brownish-yellow, and red, and becomes a fine blue on the addition of a small amount of *nitric acid* or *bromine water* (**Grandeau's reaction**), or of *ferric chloride*. *Digitaleine* gives a reddish solution with concentrated sulphuric acid, and in Grandeau's reaction a violet coloration, which changes to emerald green on dilution with water. *Digitalin Homolle* is dissolved by concentrated sulphuric acid, to form a brownish-black solution, which gradually changes to brownish-red and finally to scarlet. *German digitaline* gives a reddish-brown solution with concentrated sulphuric acid, the colour changing after some time into cherry-red. The solution gives Grandeau's reaction, the colour becoming green on the addition of water.

C. Binz's[2] method of applying Grandeau's reaction is to treat the substance in a test-tube with 3 c.c. of concentrated sulphuric acid and three drops of cold saturated bromine water. In his experience Grandeau's reaction is by no means characteristic of the digitalis glucosides. It is also obtained, *e.g.* with saponine, salicine, benzaldehyde, oil of turpentine, camphor, veratrine, brucine, and many other substances

6. *Lafon's reaction.*[3] A small quantity of the glucoside is moistened with a mixture of equal parts of *concentrated sulphuric acid* and *alcohol*, and the mixture heated until a yellow coloration appears, and then treated with a drop of *ferric chloride solution*. *Digitoxine* and *digitalin Homolle* give a bluish-green coloration, whilst, according to Dragendorff,[4] *German digitaline* does not give the reaction.

7. *Kiliani's reaction.*[5] A little of the glucoside powder under examination is treated with 4 to 5 c.c. of a mixture of 100 c.c. of pure **concentrated sulphuric acid,** to which has been added 1 c.c. of a **ferric sulphate solution** prepared by dissolving 5 grms. of commercial pure ferric sulphate in 100 c.c. of water. The lumps formed under the influence of the acid are finely divided by means of a glass rod, and so made to dissolve. The following phenomena are observed: *Digitoxine* immediately becomes quite dark, as though completely carbonised; a clear dirty brownish-red solution is then formed. *Digitonine* does not produce any coloration, and even

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[1] *Zeitsch. anal. Chem.*, **35**, 742, (1896).

[2] *Ibid.*, **45**, 144 (1906); **50**, 68 (1911).

[3] *Ibid.*, **25**, 567 (1886).

[4] *Ibid.*, **35**, 743 (1896).

[5] *Arch. d. Pharm.*, **234**, 273 (1896); *Zeitsch. anal. Chem.*, **36**, 71.

when large amounts of substance are used a faint yellowish tint at most is produced. *True digitaline* at first produces an intense golden-yellow coloration, and then dissolves, forming a red solution. This colour rapidly changes into a fine reddish-violet, which lasts for days. If somewhat too much glucoside was used, the whole solution remains red, but on then shaking the liquid the thinner layer which is formed on the surface will invariably show the reddish-violet coloration. According to R. Otto this reaction also enables true digitaline to be identified in *digitalin Homolle*, although in that case a pure reddish-violet coloration is not produced, owing to the presence of the digitoxine, which gives a brown coloration. In his experience, *German digitaline* also finally gives a reddish-violet coloration with the acid containing iron, although this is not so pronounced as in the case of true digitaline.

8. *Reaction of Keller and Kiliani.*[1] This reaction requires not only the **concentrated sulphuric acid containing iron** (as in 7), but also *glacial acetic acid*, to each 100 c.c. of which has been added 1 c.c. of the ferric sulphate solution described in 7 (any turbidity of the glacial acetic acid caused by the addition does not interfere with the test). A trace of the glucoside under examination is dissolved in 3 to 4 c.c. of the glacial acetic acid containing iron, and an equal volume of sulphuric acid containing iron is introduced beneath the liquid. In the presence of *digitoxine* a very dark zone is immediately produced at the junction of the two layers; after about two minutes a blue streak is formed above this, and after standing about 30 minutes the whole of the glacial acetic acid shows a deep indigo-blue coloration. In the course of several hours this colour changes to a pronounced bluish-green. The sulphuric acid, however, shows little, if any, coloration. *Digitonine* does not give any coloration in this test.[2] *True digitaline*, under the same conditions, imparts a coloration only to the sulphuric acid, and behaves in the same way as in the absence of glacial acetic acid (*cf.* 7). *Digitaleine* is said to be recognisable by the formation of an intense red zone. A mixture of true digitaline and digitoxine, as also *digitalin Homolle*, gives a reddish-violet coloration to the sulphuric acid, while simultaneously the glacial acetic acid becomes indigo-blue. *German digitaline* gives a coloration only to the sulphuric acid, but not to the glacial acetic acid (R. Otto [3]).

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[1] *Arch. d. Pharm.*, **234**, 275 (1896); *Zeitsch. anal. Chem.*, **36**, 72.

[2] *Zeitsch. anal. Chem.*, **36**, 72 (1897).

[3] *Anleitung zur Ausmittelung der Gifte*, 7th ed., p. 287 (1896).

Certain preparations of cinchona bark also give a similar reaction, which is to be attributed to the tannic acid contained in them, since the pure alkaloids do not show the reaction (Beitter [1]).

9. A solution of 0·5 grm. of *selenious acid* (H_2SeO_3) in 100 grms. of *concentrated sulphuric acid* gives with Merck's "pure digitaline" a yellow coloration in the cold, the colour immediately changing to red, and then gradually fading. When heated, the solution becomes bluish-violet and then brown (Mecke [2]).

10. *Pettenkofer's gall reaction.*[3] A trace of purified *ox-gall* (the officinal preparation) is dissolved in a little *concentrated sulphuric acid* in a small porcelain basin, care being taken that the temperature does not exceed 60° to 70°. The solution under examination is then added, drop by drop, while the liquid is carefully stirred with a glass rod. *True digitaline* gives a fine red coloration, as does also *digitaleine*, but not *digitoxine*. Fundamentally, the reaction is produced by the sugar liberated from the glucoside; hence, it is also obtained with other glucosides, with sugar, and with furfural.

11. *Trapp's reaction* When digitaline (no further differentiation is indicated) is treated with 5 c.c. of water, the same amount of *phosphomolybdic acid solution* added, and the mixture heated on the water bath until a green coloration appears, and then cooled and treated with ammonium chloride, a blue coloration is produced. If the liquid is then again heated on the water bath, it is decolorised. The reaction is also given by many other substances, as, for example, saponine, morphine, heroine, strychnine, aniline hydrochloride, phenacetin, etc. (C. Binz [4]).

12. A drop of a fairly *concentrated solution of cobaltous nitrate* is placed on an object glass and allowed to evaporate at a gentle heat, until a deep blue coloration is produced. If this residue is moistened with glacial acetic acid, rubbed with *digitonine*, and the moist mass allowed to stand, it becomes hygroscopic, and again assumes the red colour of cobaltous nitrate. After standing for 24 to 36 hours exposed to the air, large well-formed pink crystals separate from the deliquescent mass; when examined under a moderate magnification these are seen to consist of transparent hexagons (C. Reichard [5]).

13. The most important test for digitalis poisoning is a *physiological experiment*. Digitalis cardiac poisons, when subcutaneously

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[1] *Zeitsch. anal. Chem.*, **38**, 541 (1899).
[2] *Zeitsch. öffentl. Chem.*, **5**, 351 (1899).
[3] *Ann. d. Chem.*. **52**, 90 (1844).
[4] *Zeitsch. anal. Chem.*, **45**, 144 and 785 (1906).
[5] *Ibid.*, **56**, 175 (1917).

injected in aqueous solution into a frog, cause, even in a dose of about 1 mgrm., retardation of the action of the heart, and arrest of the heart in systole, *i.e.* stoppage during a contraction phase of the heart's pulsation.

SEC. 227.

3. Picrotoxine, $C_{30}H_{34}O_{13}$.

1. Picrotoxine is the poisonous principle of *Cocculus indicus*, the seeds of the so-called Indian berry, *Anamirta paniculata* (*Nat. Ord. Menispermaceæ*). It is not an individual chemical substance, but a complex—probably mixed crystals—of two substances which crystallise together—*picrotoxine*, $C_{15}H_{16}O_6$, and *picrotine*, $C_{15}H_{18}O_7$ (Meyer [1])—and may be dissociated by treatment with benzene, and still more readily with chloroform (E. Schmidt [2]). Picrotoxine has a poisonous action, and is the main representative of the so-called "brain-convulsion poisons." The toxic action is associated with the picrotoxinine group ; picrotine is not poisonous. Picrotoxinine is stated to show all the chemical reactions of picrotoxine.

Picrotoxine crystallises in colourless needles usually grouped into stars. It is odourless and has a neutral reaction, but has a very bitter taste. It is soluble in 350 parts of water at 20°, and in 25 parts of hot water. On cooling or evaporating its aqueous solution, it crystallises in needles. It dissolves readily in hot alcohol. A concentrated solution forms a lustrous mass on cooling, whilst dilute solutions leave lustrous needles when evaporated. Picrotoxine dissolves with difficulty in ether and chloroform, but fairly readily in amyl alcohol and glacial acetic acid. Picrotoxine is extracted from its acidified aqueous solutions by shaking with ether, chloroform, or amyl alcohol (but not with benzene or petroleum spirit). On the other hand, it is only extracted in traces from alkaline solutions by ether, chloroform, or amyl alcohol. On evaporating the ethereal solution the picrotoxine is left in the form of a powder or crystalline scales. It is lævo-rotatory : $[\alpha]_D$=about $-30°$ (in alcoholic solution). It melts at 199°–200°, and on melting yields inflammable vapours.

2. *Acids* do not neutralise picrotoxine ; nor, with the exception of acetic acid, do they increase its solubility in water.

3. *Potassium hydroxide, sodium hydroxide*, and *ammonia solutions* dissolve picrotoxine abundantly. Acids, including carbon dioxide,

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[1] *Ber.*, **7**, 16 (1897).

[2] *Ann. d. Chem.*, **222**, 340 (1884).

re-precipitate it from freshly-prepared solutions. Alkaline solutions of picrotoxine gradually change, even at the ordinary temperature; when heated they become yellow to yellowish-brown.

4. On treating picrotoxine with concentrated sulphuric acid it dissolves, forming a saffron-yellow solution; on now adding a trace of *potassium dichromate*, a violet-red coloration, changing finally to apple-green, is produced (Köhler). *Fröhde's reagent* (Sec. 213, 11) acts upon picrotoxine in the same way as concentrated sulphuric acid.

5. When picrotoxine is moistened with a little *concentrated nitric acid*, the mixture heated on the water bath until dry, and the residue moistened with the smallest possible quantity of *concentrated sulphuric acid*, and then treated with an excess of *strong sodium hydroxide solution*, a brick-red coloration is produced. A faint reaction is obtained even with 0·1 mgrm. The colour gradually disappears (Langley,[1] Dragendorff).

6. A solution of *ammonium vanadate* in *concentrated sulphuric acid* (1 : 100) gives a faint brown coloration with picrotoxine. The colour gradually darkens and, after a considerable time, becomes dark green.

7. Freshly-precipitated *lead hydroxide*, when shaken for a considerable time with an aqueous or alcoholic solution of picrotoxine, extracts the whole of the picrotoxine. The compound, separated by filtration, pressed between filter paper, and then treated with concentrated sulphuric acid, becomes first yellow, then, on standing for some time, yellowish-red, and, after moderate heating, violet-red (Palm). Picrotoxine is precipitated by *lead acetate* from an ammoniacal solution.

8. Slightly alkaline solutions of picrotoxine reduce *Fehling's solution*, on heating, with the separation of red cuprous oxide, and reduce ammoniacal silver nitrate solution (Sec. 225, 8), with the separation of brown to black metallic silver.

9. On heating a trace of picrotoxine with a few drops of *sodium hydroxide solution* to boiling-point, and then adding *iodine-potassium iodide solution*, drop by drop, *iodoform* is precipitated. This reaction depends upon the fact that acetone is liberated from picrotoxine (Sielisch [2]).

10. If one or two drops of a freshly-prepared 20 per cent. *solution* of *benzaldehyde* in absolute alcohol are dropped on to a trace of picrotoxine, and a drop of pure concentrated sulphuric acid is carefully added, the picrotoxine becomes distinctly red, and, on shaking the

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[1] *Zeitsch. anal. Chem.*, **2**, 404 (1863).

[2] *Ber.*, **45**, 2555 (1912).

mixture, red streaks are formed through the liquid, proceeding from the spot where the picrotoxine was placed. A blank test with benzaldehyde and sulphuric acid must not be omitted (*H. Melzer* [1]). Cholesterol and phytosterol behave like picrotoxine benzaldehyde (H. Kreis [2]). On adding a drop of a 20 per cent. solution of *anisaldehyde* in absolute alcohol to a solution of picrotoxine in concentrated suphuric acid, after the appearance of the saffron coloration in (4), the granules of the substance will be surrounded by an indigo-violet zone, gradually becoming blue.

11. *Iodine in potassium iodide solution, platinum chloride, gold chloride, picric acid,* and *tannic acid* do not precipitate picrotoxine from its solutions.[3]

12. Owing to the absence of any especially characteristic reactions for picrotoxine, a *physiological test* is of predominant importance in forensic cases. It is made by placing small fishes in a tap-water solution ot the suspected substance separated in the course of examination. If picrotoxine is present the fishes die after showing characteristic phenomena.

D. SYSTEMATIC COURSE FOR THE DETECTION OF THE ALKALOIDS DESCRIBED, AND ALSO OF SALICINE, DIGITALINE, AND PICROTOXINE.

In the following outline it is assumed that in the analytical course described in (*a*) and (*b*) one or more of the *non-volatile alkaloids, etc.,* described has been obtained in aqueous solution by means of an acid, and that the solution is free from foreign substances which could mask or otherwise influence the reactions. Subsequently, in (*c*) the most suitable methods are described for eliminating the disturbing influence of colouring matters or extractive substances, and lastly, the *volatile alkaloids* are also taken into consideration. By this means a knowledge will have been acquired of the methods to be used in the forensic examination of food, drugs, vomit, contents of the stomach, cadaveric remains, etc., in which not only is the presence of the above-mentioned disturbing foreign substances to be reckoned with, but the possibility of the presence of a far greater number of poisons than those described in Secs. 210 to 229 must also be taken into consideration.

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[1] *Zeitsch. anal. Chem.*, **37**, 351, 747 (1898).

[2] *Chem. Zeit.*, **23**, 21 (1899).

[3] With regard to other reactions of picrotoxine, *cf.* C. Reichard, *Zeitsch. anal. Chem.*, **52**, 590 (1913).

(*a*) *Detection of the specified non-volatile alkaloids in aqueous solutions in which only one of them is assumed to be present.*

SEC. 228.

1. A portion of the solution is acidified with a drop of dilute sulphuric acid, and treated with a potassium iodide solution of iodine or with phosphomolybdic acid solution.
   (*a*) *No precipitate is formed.* The absence of all alkaloids is indicated. Salicine, digitaline, and picrotoxine may possibly be present. The analysis is continued at 5.
   (*b*) *A precipitate is formed.* There is reason to conclude that an alkaloid is present. The analysis is continued at 2.
2. A portion of the aqueous solution is treated, drop by drop, with dilute potassium or sodium hydroxide solution, until the liquid is only just alkaline, then stirred and allowed to stand for some time.
   (*a*) *No precipitate is formed.* This indicates with certainty the absence of all alkaloids if the solution was concentrated; if, however, it was somewhat dilute, it may also remain clear in the presence of atropine. Further portions of the solution are, therefore, tested for atropine (if necessary after concentration by evaporation) by means of Vitali's reaction, and by heating it with sulphuric acid, or by means of gold chloride (Sec. 223, 6, 7, and 9).
   (*b*) *A precipitate is formed.* Sufficient potassium or sodium hydroxide is added, drop by drop, to render the liquid strongly alkaline, and if this does not cause it to become clear, even on standing for a considerable time, additional water is added.
      (*α*) *The precipitate disappears.* This indicates morphine, cocaine, or atropine. A fresh portion of the solution is tested with iodic acid (Sec. 213, 18).
         (*aa*) *Iodine is liberated. Morphine* is indicated. Confirmatory tests are made as in Sec. 213, 7, 9, 11, 12, and 14.
         (*bb*) *No iodine is liberated. Cocaine* or *atropine* is indicated. Tests for the former are made by decomposition with sulphuric acid, and by precipitation from a slightly acid solution by means of potassium chromate (Sec. 214, 7 and 11), and for atropine as in (*a*).

(β) *The precipitate does not disappear.* **This indicates a alkaloid of the second or third group (with the exceptio of atropine).** The analysis is continued at 3.

3. A second portion of the original solution is treated with 2 or drops of dilute sulphuric acid, and then with saturated sodiur hydrogen carbonate solution, until the acid reaction just disappears. The sides of the vessel below the liquid are the vigorously rubbed, and the mixture allowed to stand for half a hour.
   - (a) *No precipitate is formed.* The absence of narcotine an cinchonine is indicated. The analysis is continued at 4.
   - (b) *A precipitate is formed.* This indicates the presence o narcotine or cinchonine, and possibly quinine (the precipita bility of which by sodium hydrogen carbonate is entirel dependent on the state of dilution). A small portion o the original solution is treated with excess of ammoni and then shaken with not too small a quantity of eth containing about 2 per cent. of alcohol.
     - (α) *The precipitate first formed is dissolved by the ether, an two clear layers are obtained.* Narcotine or quinine present. They may be differentiated by testing fresh portion of the original solution with chlorine wat and ammonia (Sec. 216, 9, and Sec. 217, 9). If t solution becomes yellowish-red, it contains *narcotin* if green, *quinine* is present. As a confirmatory te of the presence of narcotine, Erdmann's reagent used (Sec. 216, 6), whilst the herapathite reacti is used for the identification of quinine (Sec. 21 11).
     - (β) *The precipitate first formed does not dissolve in the eth* Cinchonine is present. Confirmation is obtained determining its behaviour on heating (Sec. 218, 2), on treatment with potassium ferrocyanide (Sec. 2 10).

4. A small portion of the original substance, or of the dry resi left on evaporation of the solution, is brought into contact w concentrated sulphuric acid on a clock-glass.
   - (a) A colourless or faint pink solution is obtained, which becor bright red on the addition of nitric acid. *Brucine* indicated. Confirmation is afforded by the reaction w nitric acid and stannous chloride (Sec. 221, 6).

(*b*) A yellow solution, gradually changing to yellowish-red, blood-red, and purple-red, is obtained. *Veratrine* is indicated. For confirmation, the test with sugar is applied (Sec. 222, 9).

(*c*) A solution which remains colourless, even after some minutes, is obtained. If, on the addition of a granule of potassium dichromate, a deep bluish-violet coloration is produced, *strychnine* is indicated; if no change takes place, *quinine* is indicated. In the latter case confirmation is obtained by the thalleioquin reaction (Sec. 217, 9).

5. To ascertain whether the original solution contains salicine, digitaline, or picrotoxine, a portion of the original dry substance, or of the dry residue left on evaporation of the solution, is treated with concentrated sulphuric acid.

(*a*) The substance dissolves, forming a saffron-yellow solution; on adding a trace of potassium dichromate a violet-red, and finally an apple-green coloration is produced. *Picrotoxine* is indicated. Confirmatory tests are made with nitric acid and sodium hydroxide solution (Sec. 227, 6) and with benzaldehyde (Sec. 227, 10).

(*b*) The substance immediately becomes blood-red, and is slowly dissolved, forming a red solution. Salicine, and also digitalis glucosides, may be present.

(*α*) A fresh portion of the original substance is tested for salicine, by converting it into salicylic aldehyde, as in Sec. 225, 4.

(*β*) Kiliani's reaction with sulphuric acid containing iron (Sec. 226, 7) and with glacial acetic acid (Sec. 226, 8) is applied. *Digitalis preparations containing digitoxine* may thus be recognised by the respective colour reactions. If no coloration is produced, digitonine may be present; a test for it is made as in Sec. 226, 12.

(*c*) The substance dissolves, forming a reddish-brown solution, the colour of which changes to violet on the addition of a drop of bromine solution (Sec. 226, 5). A *digitaline preparation* is probably present; the reaction may also be produced by salicine and other substances. In this case, therefore, tests are also made as in (*b*), (*α*) and (*β*).

(b) *Detection of the specified non-volatile alkaloids, etc., in aqueou solutions in which several or all of them may possibly be present.*

SEC. 229.

1. The solution is rendered distinctly but not strongly acid witl hydrochloric acid, shaken with one half to an equal volume o freshly rectified pure ether free from alcohol, and the etherea extract separated from the aqueous layer, and allowed to evaporate in a glass dish.
   (a) *No residue is left.* True digitaline and picrotoxine ar absent. The analysis is continued at 2.
   (b) *A residue is left.* The presence of true digitaline or of picrotoxine may be inferred. The shaking of the aqueous laye with ether is repeated, in order to extract as completely a possible anything soluble in the latter, and the etherea extract separated and allowed to evaporate. The aqueou layer is treated as in 2, whilst the residue from the etherea extract, which may also contain traces of atropine, i treated as follows:
      (α) A portion is dissolved in alcohol, and the solutio allowed to evaporate. The formation of long lustrou needles radiating from a point indicates the presence o *picrotoxine*. Confirmation is obtained by the reaction given in Sec. 227, and especially the behaviour of th substance towards benzaldehyde (Sec. 227, 10).
      (β) A portion is tested for *true digitaline* by means of sulphuric acid containing iron (Sec. 226, 7).
      (γ) The most certain method of detecting traces of atropin is to determine whether the aqueous solution of th residue has an enlarging effect upon the pupil of the ey Vitali's reaction (Sec. 223, 6) may also be applied.
2. The hydrochloric acid liquid separated after the extraction wit ether is shaken with chloroform, and the chloroform extrac filtered through a small filter moistened with chloroform, an evaporated at a moderate temperature.
   (a) *No residue is left.* Narcotine, digitoxine, and true digitalin are absent. The analysis is continued at 3.
   (b) *A residue is left.* The shaking with chloroform is repeate so as to extract everything soluble therein from the aqueo layer. The latter is separated and treated as in 3. Th chloroform extracts are united and filtered, the filtrat

evaporated, and the residue taken up with a small amount of water acidified with hydrochloric acid. Any insoluble residue left may be digitoxine or true digitaline; the liquid is filtered, and the residue tested in the same way as the residue from the chloroform solution in the following paragraph (α). The hydrochloric acid solution is rendered distinctly alkaline with potassium hydroxide solution.

(α) *No precipitate is formed.* Narcotine is absent. The solution is shaken with chloroform, the chloroform extract evaporated, and the residue tested for *digitoxine* and *true digitaline* by Keller and Kiliani's reaction (Sec. 226, 9).

(β) *A precipitate is formed.* The presence of narcotine is indicated.

- (αα) The precipitate is filtered off, slightly washed, and dissolved in chloroform, and the chloroform evaporated. Confirmatory tests for *narcotine* are made as in Sec. 216, 6 and 9.
- (ββ) The filtrate from the precipitate is shaken with chloroform, and the chloroform extract evaporated. If any residue is left, it is tested for *digitoxine* and *true digitaline* as in (α).

3. A portion of the residual hydrochloric acid liquid left after the shaking with chloroform in 2 is treated with a potassium iodide solution of iodine, and another portion is treated with phosphomolybdic acid.

(*a*) *Precipitates are produced by these reagents.* The presence of alkaloids is indicated. The analysis is continued at 4.

(*b*) *No precipitates are formed.* Alkaloids are absent. The liquid is examined for salicine at 7.

4. A *small portion* of the aqueous liquid left after the extraction with chloroform in 2 is rendered just alkaline with sodium or potassium hydroxide, a note taken whether a precipitate is formed, a large excess of the alkali hydroxide solution added, and the liquid allowed to stand for a considerable time, and then diluted with a little water.

(*a*) *No precipitate is produced by potassium or sodium hydroxide solution, or any precipitate formed redissolves.* This indicates the presence of atropine, morphine, or cocaine, and the absence of all other alkaloids. A fresh portion of the neutralised aqueous solution is treated with excess of sodium or potassium hydrogen carbonate solution, stirred, and allowed to stand for some time.

(α) *No precipitate is formed.* Morphine is absent. A portion of the aqueous liquid is treated with excess of alkali hydroxide solution (with which it will remain clear or become clear again), and shaken with ether, and the ethereal extract evaporated to see whether it leaves a residue of *atropine* (Sec. 213, 6, 7, and 9). Another portion of the original still acid liquid is shaken with amyl alcohol, and the extract evaporated to see whether it leaves a residue of cocaine (Sec. 214, 11 and 18).

(β) *A precipitate is formed.* The presence of morphine is indicated. The liquid is filtered from the precipitate, which is further examined as in Sec. 213, 7, 9, 11, 12, and 18. In testing for atropine and cocaine, however, fresh portions of the original still acid liquid which has been shaken with ether as in (α), are used.

(*b*) *A precipitate is produced by sodium or potassium hydroxid which does not dissolve in excess of the precipitant, even afte standing for some time and moderate dilution.* The greate portion of the residual acid aqueous solution left from th extraction with chloroform (in 2) is also treated wit alkali hydroxide solution, and the precipitate filtered off and treated as in 5. The alkaline filtrate is shaken wit ether, allowed to stand for an hour (so that morphine which dissolves at first in the ether, may separate agai as completely as possible), the ethereal layer separate from the aqueous layer and evaporated, and the residu tested for atropine as in Sec. 213, 6, 7, 9 ; any morphine i the alkaline aqueous layer is then precipitated by th introduction of carbon dioxide (Sec. 213, 4). Furthe tests are made according to Sec. 213, 7, 9, 11, 12, and 1 In testing for cocaine a fresh portion of the original aci liquid is shaken with amyl alcohol (see (*a*) (α)).

5. The precipitate obtained in 4 (*b*) is filtered off, washed with col water, and dissolved in dilute sulphuric acid, so that the solutio contains a sight excess of acid, and the liquid rendered ju alkaline with sodium hydrogen carbonate solution, vigorousl shaken, and allowed to stand for an hour.

(*a*) *No precipitate is formed.* Cinchonine is absent. The solution is boiled until evaporated almost to dryness, and the residue is taken up with cold water. If nothing remains undissolved, the analysis is continued at 7. If, however, there is an insoluble residue, it is tested as in 6 for quinine (a small quantity of which might be present), and for strychnine, brucine, and veratrine.

(*b*) *A precipitate is formed.* This may contain cinchonine and also quinine (Sec. 228, 3 (*b*)). The liquid is filtered, the filtrate treated as in 5 (*a*), and the precipitate as follows :—

It is washed with cold water and dissolved in a little hydrochloric acid, and the solution treated with excess of ammonia, and then with not too small a quantity of ether containing 2 per cent. alcohol.

(α) *The precipitate produced dissolves completely in the ether, so that two clear layers are formed.* This indicates the absence of cinchonine and the presence of *quinine.* As a confirmatory test, the ethereal solution is evaporated, the residue dissolved in hydrochloric acid, and the thalleioquin reaction applied (Sec. 217, 9).

(β) *The precipitate produced does not dissolve or only dissolves incompletely in ether. Cinchonine* (and possibly also quinine) is present. The liquid is filtered, and the filtrate evaporated to dryness. If a residue is left, it is dissolved in hydrochloric acid, and tested for quinine by means of the thalleioquin reaction (Sec. 217, 9). The precipitate is cinchonine, and may be further examined as in Sec. 218, 10.

6. The residue, insoluble in water, obtained in 5 (*a*) by evaporating the liquid which was treated with sodium carbonate, is washed with water, and tested for quinine (a small quantity of which may be present), strychnine, brucine, and veratrine as follows :—

It is dried on the water bath, and digested with absolute alcohol.

(*a*) *It dissolves completely.* This indicates the absence of strychnine and the presence of (quinine) brucine or veratrine. For the identification of these the alcoholic solution is evaporated to dryness on the water bath, and, if quinine has already been detected, the residue is divided into two parts, one of these tested for *brucine* by means of nitric acid and stannous chloride (Sec. 221, 6), whilst the other is tested for *veratrine* by means of concentrated sulphuric acid (Sec. 222, 7). If, on the other hand, quinine has not yet been found, the residue is divided into three parts, *a*, *b*, and *c*, and *a* and *b* tested respectively for brucine and veratrine as described, whilst *c* is tested for *quinine* by means of chlorine water and ammonia. In the presence of brucine, however, *c* must be treated with absolute ether, the resulting ethereal solution evaporated, and the residue tested for quinine.

(*b*) *It does not dissolve, or at all events not completely.* The presence of *strychnine,* and possibly also of (quinine) brucine and veratrine, is indicated. The liquid is filtered, and tests for (quinine) brucine and veratrine applied to the filtrate as in 6 (*a*), whilst as a confirmatory test the precipitate is tested with sulphuric acid and potassium dichromate (Sec. 220, 8).

7. It still remains to test for *salicine.* For this purpose the remainder of the acid aqueous solution (2), which was shaken with chloroform, is treated with a little more hydrochloric acid, and boiled for some time. If no precipitate is formed, the absence of salicine is indicated, whilst the formation of a precipitate shows that it is present. Confirmation is obtained by boiling the liquid with a little potassium dichromate (Sec. 225, 4), and by testing the original substance with concentrated sulphuric acid (Sec. 225, 3).

(*c*) *Detection of alkaloids in food, cadaveric remains, and the like.*

The detection of poisons in food, in the contents of a stomach, cadaveric remains, etc., is very much more difficult than under the conditions hitherto assumed to be present, for there is no simple method of definitely deciding by means of a preliminary test whether or no poison is present. Hence, in all cases it is necessary to attempt to separate any poison which may be present from the mucilaginous, extractive, and colouring substances which accompany it in the material under examination, before it is possible to ascertain which specific poison is present.

In the following sections we give outlines of different methods which may be used for separating alkaloids from other substances and for drying them. We restrict ourselves, however, in Sec. 230

to the alkaloids described in this book, with the addition of picrotoxine and true digitaline.[1]

This scheme is therefore particularly suitable for a practical introduction to such examinations, but it is only exceptionally sufficiently comprehensive to be applicable to the detection of poisons in actual cases, *i.e.* in chemical forensic investigations, because, on the one hand, it does not deal with all the poisons possibly present, and on the other, does not take into consideration the ptomaines which may be present in cadaveric remains, etc., and may be mistaken for alkaloids.

Hence, if the case is not so simple that the examination may be restricted to the alkaloids of more frequent occurrence, special works which take into consideration all the above-mentioned points must be consulted in chemical forensic investigations of this kind.[2]

In order to give some idea of the methods of examination to be used in such cases, we give at the end of Sec. 230, and in Secs. 231 to 233, a few general details of the process.

SEC. 230.

1. J. S. Stas'[3] Method of detecting Poisonous Alkaloids, also True Digitaline and Picrotoxine, modified by J. and R. Otto.[4]

Stas' method is based upon the following principles :—

(α) Acid salts of alkaloids are soluble in water and alcohol.

(β) Neutral and acid salts of alkaloids are mostly insoluble in ether. Hence, the alkaloid salts do not, as a rule, pass into the ethereal solution when neutral or acid solutions are shaken with ether, and consequently the alkaloids pass into the aqueous solution as acid sulphuric acid salts when the ethereal solution of pure alkaloids is shaken with dilute sulphuric acid.

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[1] The consideration of the other digitalis glucosides is omitted, because otherwise the course of the examination would be rendered infinitely more complicated.

[2] In particular the following may be mentioned: Fr. Jul Otto, *Anleitung zur Ausmittelung der Gifte*, 7th ed., revised by R. Otto, Braunschweig, 1896. G. Dragendorff, *Beiträge zur gerichtlichen Chemie einzelner organischer Gifte*, Göttingen, 1872; *Beitrage zur gerichtlichen Chemie*, Petrograd, 1884; *Arch. d. Pharm.*, **233**, 612 (1895), and **234**, 55 and 81 (1896); *Gerichtlich-chemische Ermittelung von Giften*, 4th ed., Göttingen, 1895 (no new edition published). F. L. Sonnenschein, *Handbuch der gerichtlichen Chemie*, 2nd ed., revised by A. Classen, Berlin, 1881. L. Lewin, *Lehrbuch der Toxikologie*, Vienna and Leipzig, 1897. R. Kobert, *Lehrbuch der Intoxikationen*, 2 vols., Stuttgart, 1906. C. Kippenberger, *Grundlagen fur den Nachweis von Giftstoffen bei gerichtlich-chemischen Untersuchungen*, Berlin, 1897. G. Baumert, M. Dennstedt, and F. Voigtländer, *Lehrbuch der gerichtlichen Chemie*, 2 vols., Braunschweig, 1906 to 1907. J. Gadamer, *Lehrbuch der chemischen Toxikologie und Anleitung zur Ausmittelung der Gifte*, Göttingen, 1909. W. Autenrieth, *Die Auffindung der Gifte und stark wirkenden Arzneistoffe*, 4th ed., Tübingen, 1909. C. Ipsen, *Der chemische Giftnachweis*, Wiesbaden, 1914. With regard to *ptomaines*, *cf.* the comprehensive statements of Otto on pp. 100 to 118 of his book mentioned above, and those on pp. 631 to 662 of Gadamer's book.

[3] *Bull. de l'Acad. Med. Belg.*, **2**, 304; *Jahrb. prakt. Pharm.*, **24**, 313; *Jahresber. von Liebig and Kopp*, 1851, 640.

[4] *Ann. d. Chem.*, **100**, 44; Fr. Jul. Otto, *Anleitung zur Ausmittelung der Gifte*, 7th ed., revised by R. Otto, pp. 118 *et seq.*, Braunschweig.

(γ) If aqueous solutions containing neutral or acid salts of the alkaloids are treated with pure alkali carbonates, or alkali hydrogen carbonates, the alkaloids are liberated, and if then shaken with ether or amyl alcohol, the pure alkaloids pass into the ethereal or amyl alcohol solutions respectively.

The few exceptions to these general principles may be gathered from the following remarks :—

(*a*) If the alkaloid is to be detected in the contents of a stomach or intestine, in food, or pasty substances generally, these are heated beneath a reflux condenser at 70°–79 ° with twice their volume by weight of strong pure alcohol (previously rectified over tartaric acid), sufficient tartaric acid being added to give the liquid a distinctly acid reaction (a greater excess must be avoided). When quite cold, the mixture is filtered, and anything that has remained undissolved washed with strong pure alcohol.

If the bases are to be detected in the heart, liver, lungs, or similar organs, these should be cut up into small pieces, digested with alcohol which has been acidified in the manner described above, and pressed, and this treatment repeated until everything soluble has been extracted ; the combined liquids, when absolutely cold, are filtered.

(*b*) The alcoholic liquids are now concentrated by evaporation at a low temperature. This can be done in a porcelain dish on the water bath, the water of which is not allowed to exceed about 80°. The temperature of the contents of the dish will then not exceed 40°–50°. If it is desired to keep the temperature still lower, the evaporation is accelerated as much as possible by blowing air diagonally on to the surface of the liquid. According to Stas the temperature should not exceed 35°. He therefore suggests carrying out the evaporation in a desiccator over sulphuric acid, with or without the aid of a vacuum, or else in a retort, through the tubulure of which a current of air is introduced.

Such a precaution, however, is only necessary under exceptional conditions, and in any case the main quantity of the liquid may first be evaporated on a moderately heated water bath.

If, in the evaporation, insoluble substances, fat, etc., separate (which is generally the case), the solution freed from alcohol by evaporation is filtered through a filter moistened with water, and the filtrate, together with the washings, evaporated by one of the methods described above, until it is of the consistency of an extract. If no insoluble substances separate on the evaporation of the alcoholic liquid. the evaporation to such consistency may be effected beforehand.

(*c*) The residue from the evaporation is treated with successive small quantities of cold absolute alcohol, to effect complete extraction, thoroughly mixed, and finally a large amount of alcohol added, in order that everything precipitable in it may separate. The alcoholic extract is filtered through a filter moistened with alcohol, the residue washed with cold alcohol, the alcoholic solution allowed to evaporate at not too high a temperature (*vide supra*), the residual acid residue taken up with a little water, and the acid solution shaken with ether (after the greater portion of the free acid has been neutralised with dilute sodium hydroxide solution), so that the reaction is slightly but *distinctly acid.* The ethereal layer is separated from the aqueous layer by means of a separating funnel or a burette provided with a glass tap, the acid aqueous solution repeated by shaken with ether until the last ethereal extracts appear colourless. In this process it is better to use a cylindrical rather than the ordinary globular separating funnel.

Of the alkaloids, etc., under consideration here, the ether extracts, apart from colouring substances, picrotoxine and true digitaline, and also traces of veratrine and atropine. It is advisable to reserve the first strongly coloured and the last less strongly coloured ethereal solutions for further examination (*cf.* (*h*)).

(*d*) The aqueous acid solution, separated from the ether, is gently heated, in order to free it from the still dissolved ether, and then carefully treated with sodium hydroxide solution until turmeric paper becomes decidedly brown.

The alkaloids are thus liberated, and any morphine present dissolves in the excess of sodium hydroxide solution. The alkaline liquid is shaken with pure ether and, after an hour, the ethereal extracts separated from the aqueous liquid as in (*c*). The ethereal extract now contains all the alkaloids present, with the exception of morphine, only a small portion of which passes into the ethereal solution. The quantity is smaller the more completely the acid aqueous solution was freed from the ether dissolved in it, and the longer the time that elapsed between the shaking with ether and the separation of the ethereal layer from the aqueous liquid. A portion of the ethereal extract is next allowed to evaporate on a large clock-glass, which is placed on a surface heated to 20° or 30°, in order to prevent condensation of water. If no residue is left, no alkaloid has dissolved in the ethereal solution, and the process is continued at (*g*); if, however, a residue does remain, numerous conclusions may be drawn from its character. In particular, oily streaks on the clock-glass, which gradually agglomerate to form a drop, and which on heating emit an unpleasant penetrating and suffocating odour, point to a liquid volatile alkaloid, whereas a solid residue, or a turbid liquid in which solid particles are suspended, lead to the assumption that a non-volatile solid alkaloid is present. First of all, the aqueous solution, rendered alkaline, is again shaken with a fairly large quantity of ether (provided the ethereal extract yielded a residue) until a sample of the last ethereal extract no longer leaves a residue on evaporation. The combined ethereal extracts are then evaporated in a small glass dish on the water bath (containing water at about 30°), and as the liquid evaporates the dish is repeatedly filled up.

The aqueous alkaline solution, which contains any morphine that may be present, is separated from the ethereal extracts and examined as in (*g*).

(*e*) If the acid aqueous solution has been thoroughly and completely extracted with ether in (*c*), the alkaloids are left in so pure a condition after evaporating the ethereal extract obtained in (*d*) that the residue may be used directly for the purpose of tests. In particular, the portions which remain in the deepest part of the dish are purer than the rings formed above it. If the residue is left in oily streaks or drops, the dish is finally placed in a vacuum over sulphuric acid, in order to remove the last portions of ether and ammonia, and the residue tested for coniine and nicotine as in Sec. 212. If it is crystalline, it is examined under the microscope, and then tested as in Sec. 228 or 229, provided the characteristics of the crystals do not justify a direct test for a definite alkaloid. It must be noted, however, that, if all the extractions in Sec. 229 were not carried out, tests for narcotine must be applied in another place than that chosen in Sec. 229 when the course of extraction selected here is used. It may be found with the quinine in the ethereal solution of Sec. 229, 5 (*b*) (*a*). This ethereal solution is evaporated, and the residue taken up with a little hydrochloric acid and sufficient water to dilute the liquid to at least 1 : 200; sodium hydrogen carbonate is then added until the reaction is neutral, and the liquid allowed to stand for some time. A precipitate indicates narcotine; confirmation may be obtained as in Sec. 216, 6 and 9. The liquid, still clear or else filtered from the precipitate, is evaporated to dryness, and treated with water. Any undissolved particles left are dissolved in hydrochloric acid and tested for quinine by means of the thalleioquin reaction (Sec. 217, 9).

If the residue left on the evaporation of the ethereal extract obtained in (*d*) does not form oily streaks or distinct crystals, but amorphous rings (which may happen if the evaporation was carried out too rapidly with the aid of heat), they are dissolved in a little warm absolute alcohol, the solution slowly evaporated, and note taken whether small crystals are then formed, and the treatment of the residue continued as described above.

(*f*) If, however, the acid aqueous liquid was not completely extracted with ether in (*c*), the residue obtained on evaporating the ethereal extract derived from the alkaline solution will often not be sufficiently pure to be subjected to direct examination. In that case, it is dissolved in water (acidified with a little sulphuric acid), the solution filtered if necessary, and the acid filtrate shaken repeatedly with ether. (The ethereal solution thus obtained may contain the remainder of the true digitaline and picrotoxine, and should be examined as in (*h*) in the same way as that obtained in (*c*).) The aqueous solution (after it has been freed from dissolved ether by gentle heating) is next treated with a considerable excess of potassium or sodium hydroxide, and repeatedly shaken with ether (the precautionary measures mentioned in (*d*) being observed) until the last extract no longer leaves a residue on evaporation. The ethereal extracts are evaporated as described in (*d*), and the alkaloid residue, now pure, treated as in (*e*),[1] whilst the aqueous alkaline solution, which may contain traces of morphine, is combined with that obtained in (*d*).

(*g*) The aqueous alkaline liquid obtained in (*d*) or in (*d*) and (*f*), in which all or the greater part of any morphine present must be contained, is freed by gentle heating from the ether dissolved in it, and treated, first with hydrochloric acid until the reaction is acid, then with an excess of ammonia, and directly afterwards with freshly-rectified pure amyl alcohol,[2] and then shaken. Since morphine dissolves more readily in hot than in cold amyl alcohol, it is advisable to heat the solution by dipping the flask in hot water, then to add the amyl alcohol, to close the flask, to shake it (lifting the stopper occasionally), and to pour the whole contents of the flask into a separating funnel. After the layer of amyl alcohol has been separated from the aqueous solution, the ammoniacal liquid is again shaken with amyl alcohol. The combined amyl alcohol extracts, completely freed from water by allowing the liquid to subside and filtering it, are evaporated, and the residue, if any, tested according to Sec. 213 for morphine. If this residue was not sufficiently pure, it is purified by re-dissolving it in

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[1] In the event of strychnine still not being obtained absolutely pure by this method, Fr. Janssens (*Zeitsch. anal. Chem.*, 4, 48 (1865)) recommends re-dissolving it in dilute tartaric acid solution, and, while shaking it, adding sufficient finely powdered sodium hydrogen carbonate to ensure that the acidity of the liquid is only due to free carbonic acid. Should a precipitate separate, it is at once filtered off through a rapid filter. The strychnine remains dissolved, owing to the action of the free carbon dioxide, and only separates when the filtrate is boiled and partly evaporated. When *this* precipitate has been filtered off and washed it is dissolved in a small quantity of dilute sulphuric acid (1 : 200), potassium carbonate added in excess, the liquid shaken repeatedly with six times its volume of ether, and the extract evaporated. Chloroform is even better than ether for extracting the alkaline solution.

[2] The amyl alcohol should have a boiling point of 131°. When evaporated on the water bath it should not leave any appreciable residue, and when shaken with water containing sulphuric acid should not yield any substances which give precipitates with reagents for the precipitation of alkaloids.